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**FINAL REPORT**  
Covering the Period July 10, 1978 to January 31, 1981

on

**EVALUATION OF SELECTED CHEMICAL PROCESSES  
FOR PRODUCTION OF LOW-COST SILICON**

(Phase III)

JPL Contract 954339

Silicon Material Task  
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

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March 31, 1981

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## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT . . . . .	1
ABSTRACT . . . . .	1
SUMMARY . . . . .	3
INTRODUCTION . . . . .	7
DESIGN OF THE EPSDU . . . . .	8
ECCNOMIC ANALYSIS OF SILICON PRODUCTION AT THE 1000 MT/YEAR LEVEL .	17
ENERGY PAY-BACK . . . . .	19
PROCESS DEVELOPMENT UNIT . . . . .	22
PDU OPERATION . . . . .	36
PDU Start-up and Operating Procedures . . . . .	38
PDU Operating Experience . . . . .	45
Status of Operability of the Four Critical PDU Units . . . . .	51
PROCESS DISCUSSION . . . . .	60
RECOMMENDATIONS . . . . .	63
EXPERIMENTAL SUPPORT . . . . .	64
Product Quality . . . . .	64
Elimination of Residual Zinc . . . . .	65
Prospects for Decreasing the Residual Zinc Content of the	
Product . . . . .	67
Implications of Not Removing the Zinc . . . . .	68
Heat Treatment Experiments . . . . .	69
Results of the Heat Treatment Data . . . . .	71
Vaporization of Zinc . . . . .	77

TABLE OF CONTENTS, Cont.

	<u>Page</u>
Direct Coupled Zinc Vaporizer . . . . .	80
Segregation of "Large" Particles in the Fluidized-Bed Reactor . . . . .	81
Electrolysis of $ZnCl_2$ . . . . .	84
Wetted-Wall Condenser Studies . . . . .	90
REFERENCES . . . . .	96



## LIST OF FIGURES

	<u>Page</u>
Figure 1. $\text{SiCl}_4$ Purification System . . . . .	9
Figure 2. Reactor-Recovery System . . . . .	10
Figure 3. Waste Treatment System . . . . .	11
Figure 4. Silicon Tetrachloride Storage and Purification . . . . .	12
Figure 5. Fluidized-Bed Reactors . . . . .	13
Figure 6. Recovery-Recycle Section . . . . .	14
Figure 7. Waste Disposal Area . . . . .	15
Figure 8a. PDU Flow Diagram, Reaction Section . . . . .	23
Figure 8b. PDU Flow Diagram, Reaction-Product Treatment Section . . . . .	24
Figure 8c. PDU Flow Diagram, Heat-Transfer System . . . . .	25
Figure 9. Process Development Unit (PDU) . . . . .	27
Figure 10. 7.0"-ID Fluidized-Bed Reactor . . . . .	28
Figure 11. Zinc Vaporizer . . . . .	30
Figure 12. Zinc/ $\text{ZnCl}_2$ Condenser . . . . .	32
Figure 13. Electrolytic Cell . . . . .	33
Figure 14. Alternative Zinc Feed System . . . . .	52
Figure 15. Graphite Tray Zinc Vaporizer . . . . .	53
Figure 16. Liquid Zinc Displacement Feeder . . . . .	54
Figure 17. Miniplant Product Granules . . . . .	66
Figure 18. Diagram of Round-Bottom Distributor Used in Model Studies . . . . .	82
Figure 19. Schematic Diagram of Laboratory-Scale Wet-Wall Condenser . . . . .	93

## LIST OF TABLES

	<u>Page</u>
Table 1. Selling Price of Silicon for Various Levels of Return of Investment . . . . .	18
Table 2. Energy Requirements, kwh/kg Silicon . . . . .	21
Table 3. PDU Procedures . . . . .	39
Table 4. PDU Operation History . . . . .	46
Table 5. Modifications of PDU Equipment and Operation . . . . .	48
Table 6. Mercury Porosimeter Measurement of Run-50 Material After 256 Hours in Vacuum at 900 C . . . . .	72
Table 7. Times to Outgas Granules in Accordance with Model C . . .	75
Table 8. Data and Calculated Relative Volatilities, Experiment A . . . . .	78
Table 9. Data and Calculated Relative Volatilities, Experiment B . . . . .	79
Table 10. Particle Size Distribution for Segregation Experiments in Fluidized-Bed Model . . . . .	83
Table 11. Summary of ZnCl <sub>2</sub> By-Product Electrolysis Experiments at 500 C . . . . .	87
Table 12. Summary of Additional ZnCl <sub>2</sub> By-Product Electrolysis Experiments at 500 C . . . . .	89

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ABSTRACT

As a phase of a program to establish the engineering feasibility of the process for producing silicon by the zinc vapor reduction of silicon tetrachloride, a Process Development Unit (PDU), which consisted of the four major units of the process, was designed, installed, and experimentally operated. The PDU was sized to 50MT/Yr. The deposition took place in a fluidized bed reactor. As a consequence of the experiments, improvements in the design and operation of these units were undertaken and their experimental limitations were partially established.

A parallel program of experimental work demonstrated that

- (1) Zinc can be vaporized for introduction into the fluidized bed reactor, by direct induction-coupled r.f. energy.

- (2) Residual zinc in the product, expected to be of the order of 100 ppm by weight, can be removed by heat treatment below the melting point of silicon. However, deferring the zinc removal until the silicon is melted in the sheet-forming process is shown to be an attractive option.
- (3) Current efficiencies of 94 percent and above, and power efficiencies around 40 percent are achievable in the laboratory-scale electrolysis of  $\text{ZnCl}_2$  (50 m/o in  $\text{KCl}$ ).

Independent work at Westinghouse has established that photovoltaic cells with 13 percent efficiency could be made with web dendrites formed from the product.

Work with the PDU has revealed no fundamental barriers to the commercialization of the fluidized-bed zinc-reduction process for silicon. However, successful implementation of the process will depend on appropriate engineering solutions to problems remaining at the end of the PDU program.

## SUMMARY

The Battelle process for the production of low-cost high-purity silicon is based on the zinc-vapor reduction of silicon tetrachloride in a fluidized bed of seed particles at about 925 C.\* The seed particles grow by the deposition of silicon to yield a free-flowing granular product which is well adapted to continuous feeding in ingot- or sheet-growth processes. The by-product zinc chloride is condensed and subjected to fused-salt electrolysis to recover the zinc and chlorine for recycle.

Experimental solar cells, fabricated by Westinghouse from web dendrites grown from the Battelle product, exhibited efficiencies of 13 percent (Air Mass 1), corrected to include an antireflective layer. Although useful in its present form, the product is subject to improvement by (1) identification and removal of the cause of some auto doping detected in the work by Westinghouse, and (2) the elimination of some 100 ppmw of residual zinc, which does not appear to affect the electrical properties but which contributes a small (e.g., 5 volume per cent) increase in the volatiles [mainly SiO(g)] from the ingot- or sheet-growth step.

Removal of most of the residual zinc by heat treatment at temperatures (e.g., 1050-1100 C) below the melting point of silicon has been shown to be effective. However, the amount of zinc is so small relative to that of the SiO given off in a typical Czochralski crystal growth, for example, that one is attracted to the alternative of relying on the automatic evolution that occurs when the silicon is melted in the ingot- or sheet-growth process.

Battelle estimates of the selling price (20% R.O.I) of silicon produced by the process at the 1000 MT/yr level are as low as \$14.80 (\$ 1980) depending upon the size and multiplicity of fluidized

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\* Operation below 915 C results in condensation of zinc, and operation above 925 results in a decrease in reaction efficiency by about 0.1 percent per degree from the 63 percent reference efficiency at 925 C.

bed reactors and electrolytic cells assumed. Thus, the economics of the process for at least one set of assumptions is in the range of the LSA target selling price of \$14/kg (\$1980).

The energy consumption (56.7 kwh/kg Si) of the production process is moderate, leading to a break-even point at 4.5 months' operation for a 10-percent-efficient solar cell, 0.0254 cm in thickness with a silicon utilization efficiency of 50 percent.

In the light of the above information, it is probable that the Battelle process can meet the LSA project goals with respect to product quality and price. However, many aspects of the process present difficult engineering challenges that must be resolved before it becomes a routine operation. The major problems stem from having to handle the corrosive and condensible materials, zinc, and zinc chloride at high temperatures.

Many of the problems associated with the process were solved during work with the Process Development Unit (PDU) in Phase III of the Battelle program, reported here. However, operation of the PDU revealed limitations in the current design of the fluidized-bed reactor which in turn prevented a full evaluation of the other critical units of the process, whose design the PDU was intended to validate.

Appropriate sealing of the graphite liner of the fluidized-bed reactor in its stainless steel shell and purging of the annulus were provided to prevent access of zinc and zinc chloride to the stainless steel. Further, appropriate precautions were taken to provide for the large predictable thermal expansion differential between the graphite and the stainless steel. However, unpredictable movements of the shell relative to the liner (relaxation of residual stress?) led to the frequent breakage of appendages, and unexpected downstream constriction of the system with reaction by-products led to disruption of the purge streams, with the result that on a few occasions zinc and zinc chloride entered the annulus. This led to corrosion and penetration of the thin stainless steel bellows that were used to accommodate the axial displacement due to thermal expansion differential. Since both zinc and zinc chloride are volatile condensibles, their presence is persistent, and once having intruded, they are difficult to control or remove. Accordingly, whereas

ideally a reactor consisting of a stainless steel shell and graphite liner might eventually be made to work, it is now judged more difficult than initially thought.

Unfortunately, the range of materials compatible with the reaction mixture at 925 C is limited, graphite and quartz being the principle contenders. Since quartz is compatible with air, a lined vessel is not required thus simplifying construction. Accordingly it is recommended that in work with the process in the immediate future, attention be given to the design and use of a quartz reactor, despite its long-range size limitations.

One unfortunate result of the curtailed operation of the PDU was that the by-product condenser was not fully evaluated. Proper condensation and separation of the by-product zinc chloride and unreacted zinc from the unreacted silicon tetrachloride is a critical operation. If the by-product mixture is cooled too slowly, the silicon tetrachloride will react with liquid zinc to give silicon needles which can constrict the system downstream. If on the other hand the by-product is cooled too rapidly, zinc chloride (the major component) and zinc can fog out and be carried downstream by entrainment, again to constrict the system. Although most of the downstream constrictions observed in the PDU operation can be attributed to other factors\*, the efficiency of operation of the condenser (including the recirculation of liquid zinc chloride to wet the condenser surface) was not fully evaluated. Accordingly, subsequent work with the process should include characterization of the condenser operation. If the present condenser cannot be shown to have an operational "window" between silicon needle formation on the one hand and zinc chloride fogging on the other, quenching of the by-product mixture with recirculated silicon tetrachloride is a possible alternative, with provision being made for separating the components of the resultant slurry.

Although progress was made in ensuring the operability in the PDU of a graphite-tray "flash" vaporizer fed with metered liquid zinc,

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\* Liquid  $\text{SiCl}_4$  reaching the sparger tube in the waste disposal system (since corrected), deficient stripper design and operation (partially corrected), etc.

a zinc vaporizer energized by direct induction-coupled r.f. would appear to be preferable because of the quick response of vapor output to control signal. The use of a saturable core reactor to control the r.f. output in the induction heater in place of electronic control was found to eliminate a high voltage transient in the wave form and avoid the formation of the parasitic plasma in the zinc vapor that was observed in early attempts to operate the PDU with a direct-coupled vaporizer.

Although operation of the 6000-amp electrolytic cell was not evaluated owing to an insufficiency of by-product zinc chloride (containing zinc and silicon in suspension), it is believed in the light of experience with a similar cell as the U.S. Bureau of Mines, Reno, Nevada, that operation of the electrolytic cell should be one of the least troublesome aspects of the process. Current efficiencies of 94 percent (and over), and power efficiencies around 40 percent were demonstrated for a small (50-amp) laboratory cell in laboratory experimental work concurrent with PDU operation.

In summary, although the operation of the PDU did not reach the point of being sufficiently routine to obtain the desired engineering data, significant improvements in the process were made in Phase III and nothing was revealed that would preclude the competitiveness of an appropriately engineered facility for the production of low-cost high-purity silicon for solar cell use.

## INTRODUCTION

This final report covers Phase III of a program at Battelle Columbus Laboratories (BCL) designed to evaluate the technical and economic feasibility of the zinc vapor reduction of silicon tetrachloride in a fluidized bed of silicon seed particles as a means of producing high-purity silicon granules at low cost for use in solar arrays for power generation. The BCL program was part of the Low Cost Solar Array Project (LSA) managed by the Jet Propulsion Laboratory (JPL) for the Department of Energy (DOE).

The reader is referred to the Final Report for Phases I and II<sup>(1)</sup> in which the background is given on (1) the choice of the zinc reduction process from among several alternative processes, (2) demonstration in the "Miniplant" on a laboratory scale of the technical feasibility of the process, (3) analysis of the process costs, and (4) design of a 50-metric-ton-per-year experimental facility (EPSDU\*).

The present report covers refinements in the design of the EPSDU, and refinements in the economic analyses. Also covered are the work with a Process Development Unit (PDU) and various items of experimental work carried out in support of the PDU activity but independent of the operation of the PDU itself. The program involving the PDU was adopted as a means of assessing the operability, on an 8-hour batch basis, of four critical units of the 50 MT/year EPSDU design: the fluidized-bed reactor, the zinc/zinc chloride by-product condenser, the zinc vaporizer, and the cell for fused-salt electrolysis of the zinc chloride and recycle of the zinc and chlorine.

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\* EPSDU is an acronym for "Experimental Process System Development Facility".

## DESIGN OF THE EPSDU

The design of the 50 MT/year EPSDU was carried out under a subcontract by Raphael Katzen Associates International, Inc., (RKAI) at Cincinnati, Ohio with the cooperation of BCL personnel. Details of that design as it stood at the close of Phase II of the program are given in the Tenth Quarterly Report<sup>(2)</sup> and the Final Report for Phases I and II<sup>(1)</sup>. Only changes from the design in the Final Report are discussed here. The major alterations, made for purposes of economy or process simplifications are:

- (1) Redesign of the  $\text{ZnCl}_2/\text{Zn}$  by-product system to operate at 350 C rather than 500 C (zinc handled as a slurry of fine solid particles suspended in the  $\text{ZnCl}_2$ , rather than as a liquid).
- (2) Elimination of two of the original four  $\text{ZnCl}_2$  strippers.
- (3) Redesign of the electrodes of the cell for electrolyzing  $\text{ZnCl}_2$ .
- (4) Refinement of the design of the waste-disposal system.

These changes, as reflected in the corresponding process flow diagrams, Figures 1 through 3, are discussed in detail in the Eleventh-Twelfth Quarterly Report<sup>(3)</sup> and will not be discussed further here, except as they relate to the PDU design which is covered in a later section of this report. Because of the complexity of the EPSDU design, full details are, of course, obtainable only by reference to the original design documents<sup>(4)</sup>.

As part of the design activity, two models of the EPSDU have been made, one primarily for display purposes, consisting of only the Reactor/Recovery section of the facility [Figures 6 and 7 of the Eleventh/Twelfth Quarterly Report<sup>(3)</sup>], and the other, a 1/16 scale model of the entire facility, constructed to (1) facilitate the layout and piping phases of the design, (2) aid construction contractors in cost estimation, and (3) serve as a reference during construction. Figures 4 through 7 show four views of the latter model.

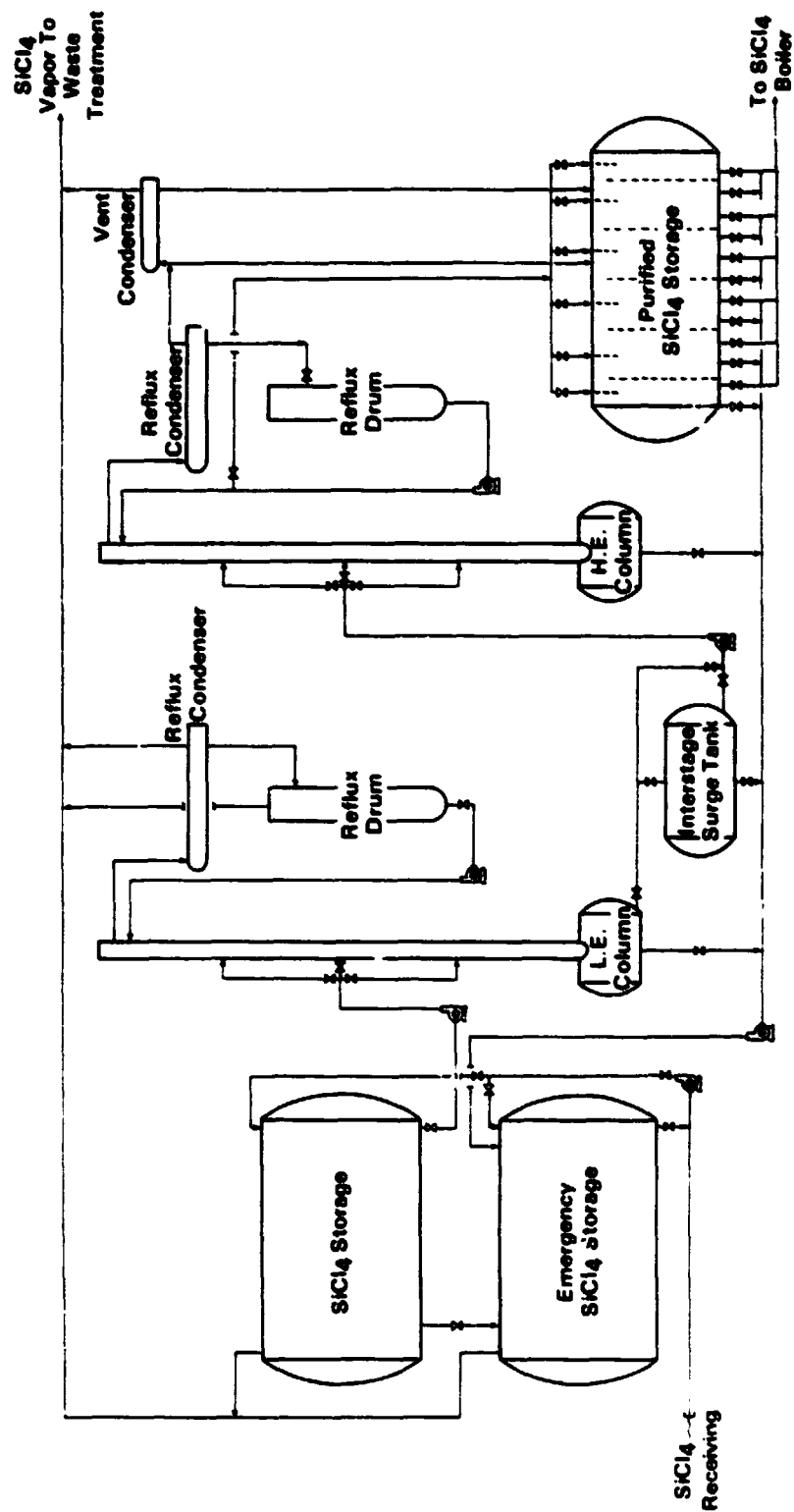


FIGURE 1. SiCl<sub>4</sub> PURIFICATION SYSTEM

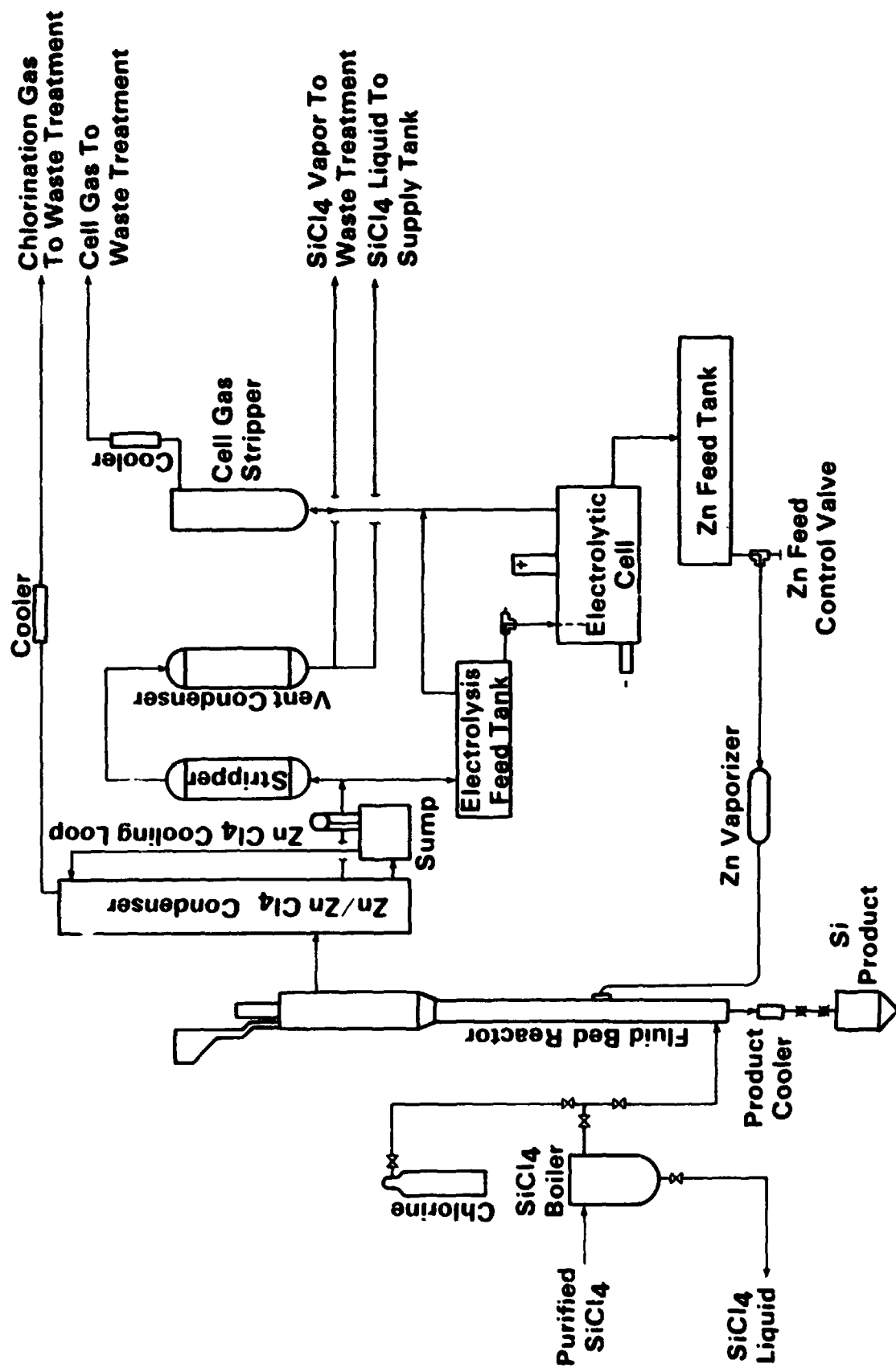


FIGURE 2. REACTOR-RECOVERY SYSTEM

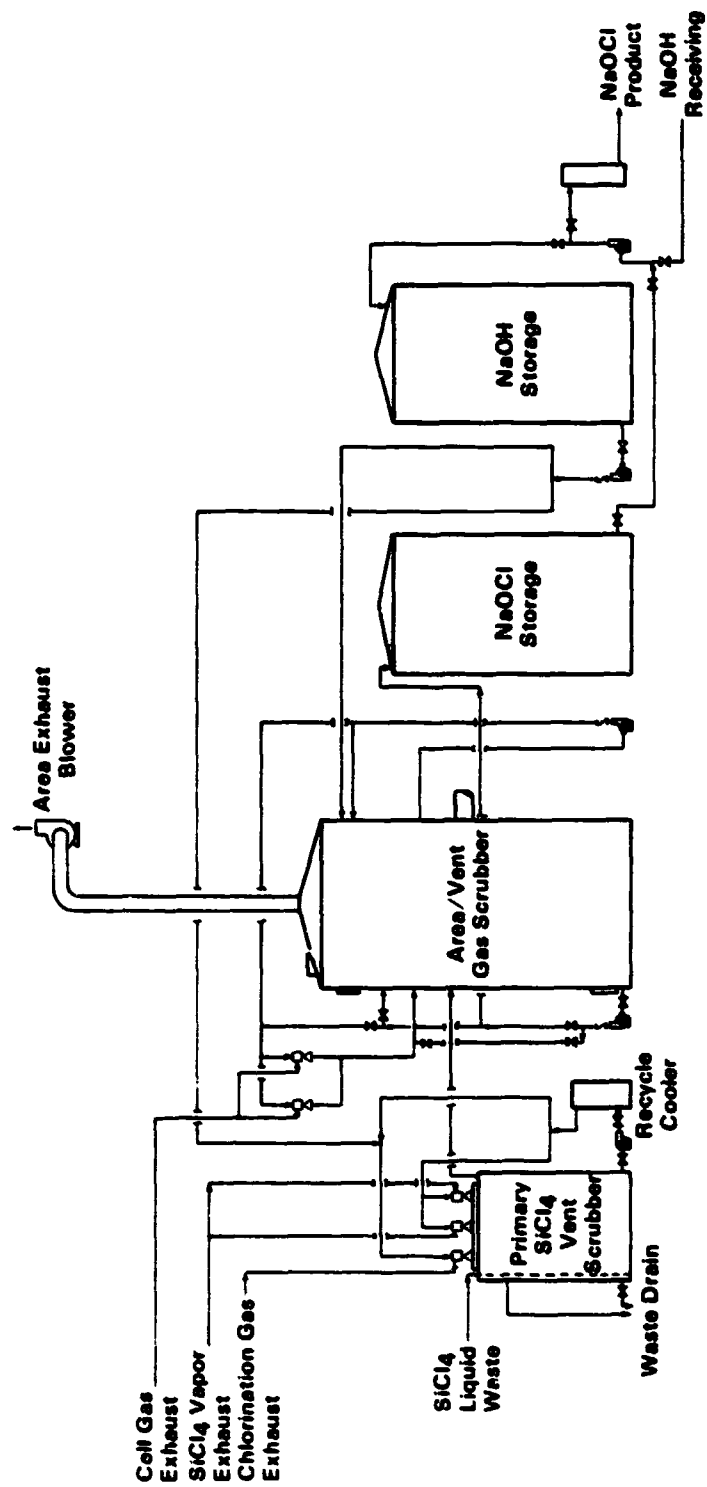


FIGURE 3. WASTE TREATMENT SYSTEM

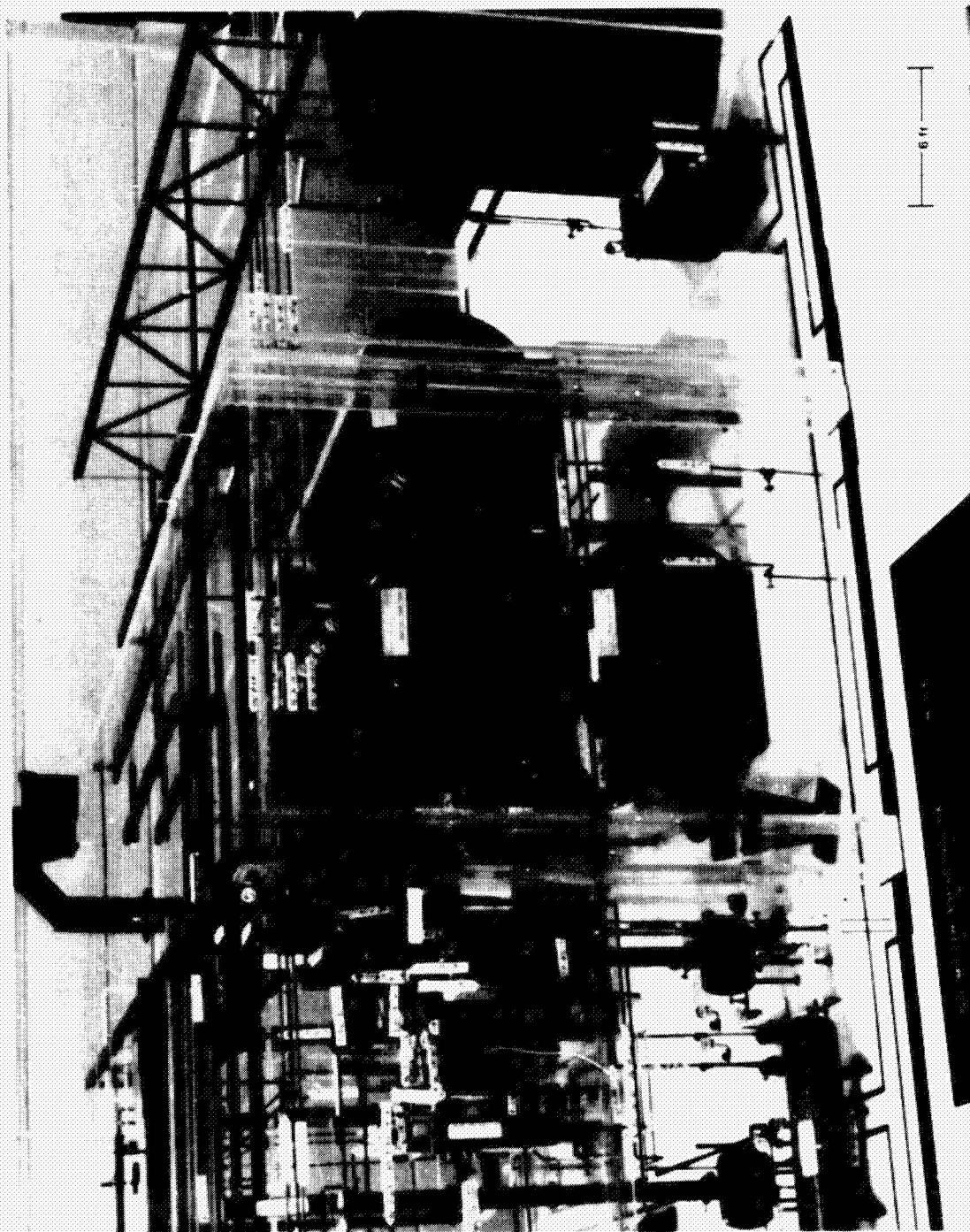


FIGURE 4. SILICON TETRACHLORIDE STORAGE AND PURIFICATION

Tanks for storage of purified and crude  $\text{SiCl}_4$  are shown in the center, upper level, with a tank for emergency  $\text{SiCl}_4$  storage below. Part of the system for purifying  $\text{SiCl}_4$  by distillation is shown on the left. Scale = 1/90

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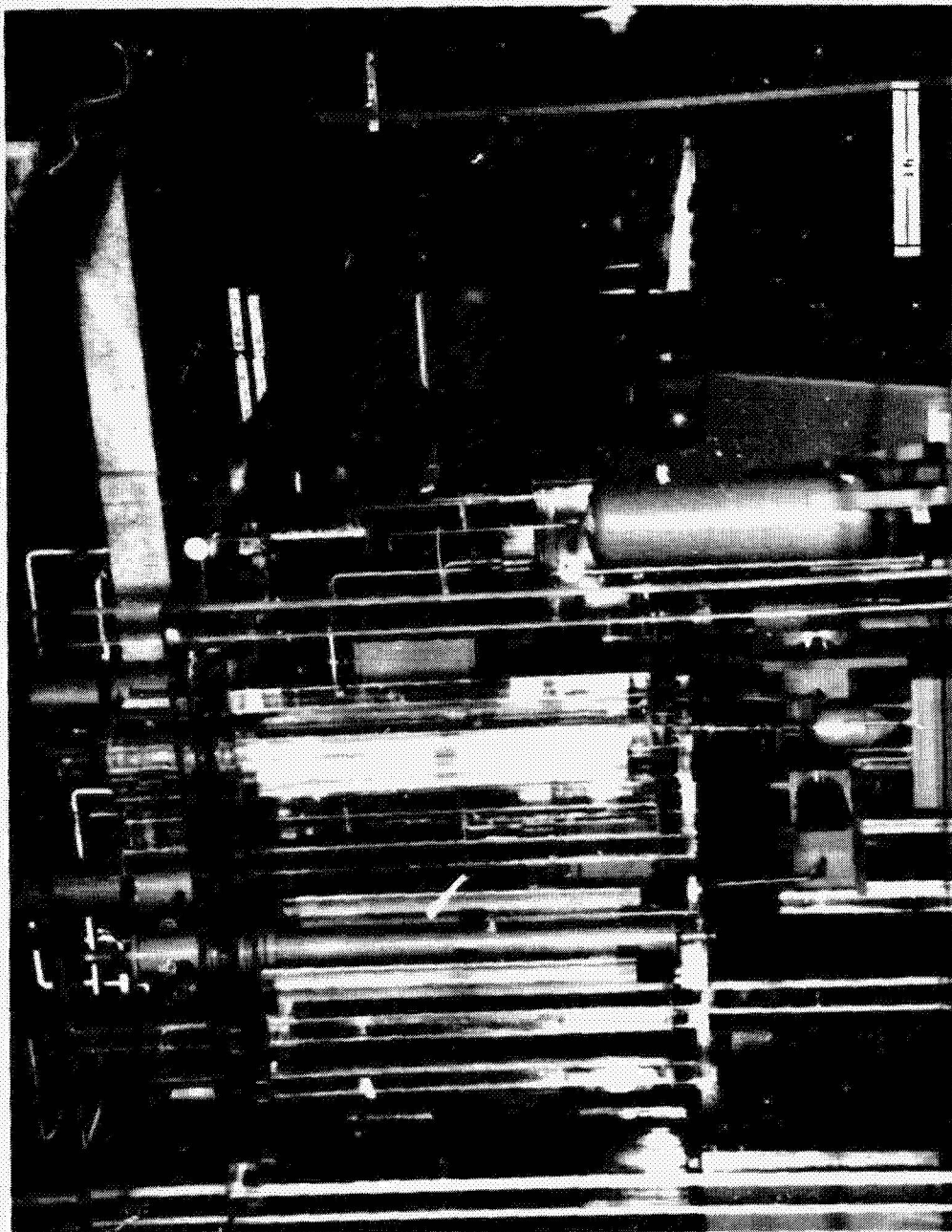


FIGURE 5. FLUIDIZED-BED REACTORS

The two vertical fluidized-bed reactors are shown left of center. The one on the right is enclosed by a (transparent) furnace and is provided with a product-withdrawal tank below. The reactor on the left has been stripped for maintenance. The zinc vaporizers are shown to the right and left just behind the product-withdrawal tank. The  $\text{SiCl}_4$  vaporizer is located beside the 6-foot model person in the right foreground. Scale = 1/40

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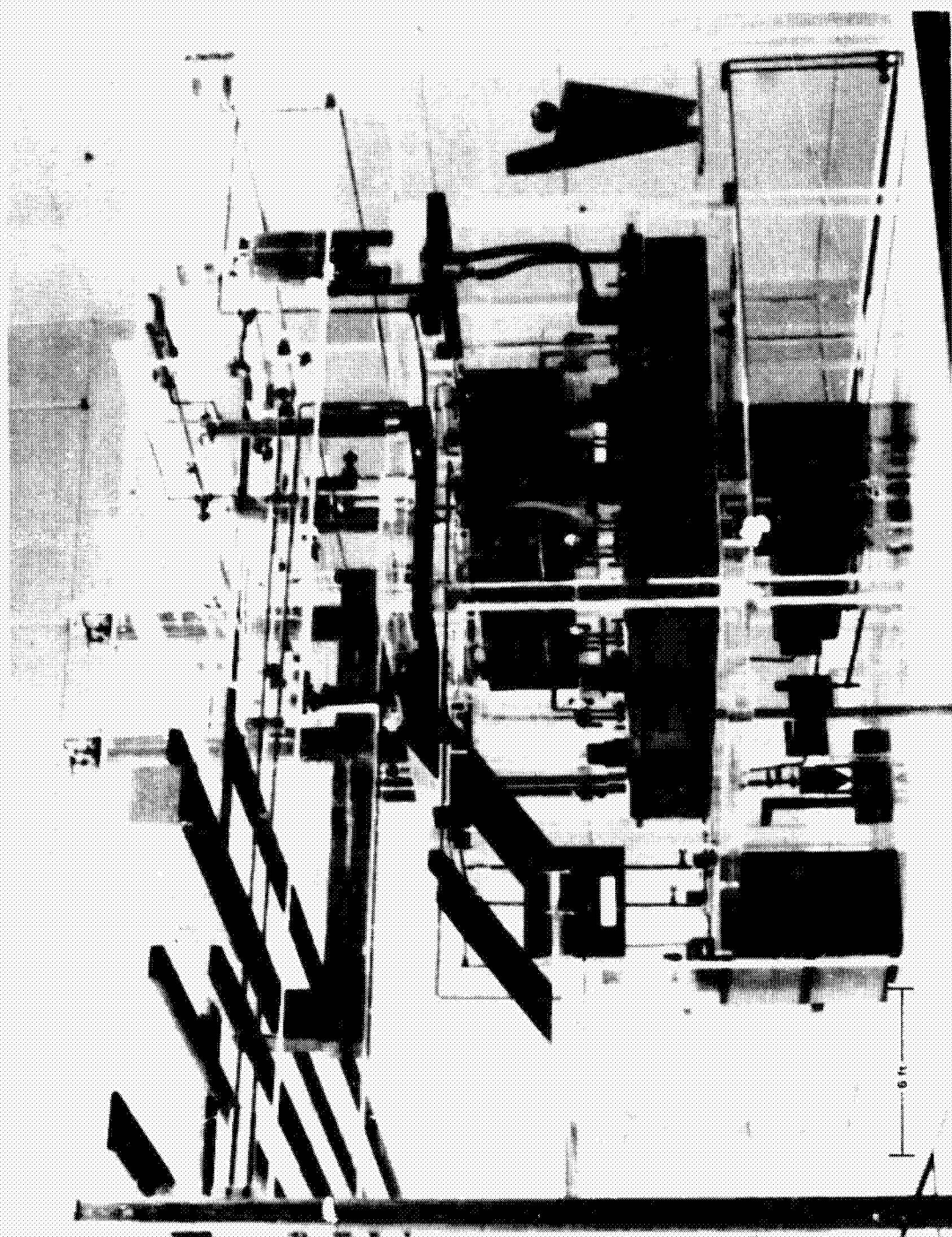


FIGURE 6. RECOVERY-RECYCLE SECTION

The vertical condensers for  $\text{ZnCl}_2$  are shown at the highest point above and to the left of the  $\text{ZnCl}_2$  storage tank in the center. Below the  $\text{ZnCl}_2$  storage tank are the electrolytic cells which feed the zinc storage tank at the lowest level. In this view, the fluidized-bed reactors are in the rear just left of center. Scale = 1/75

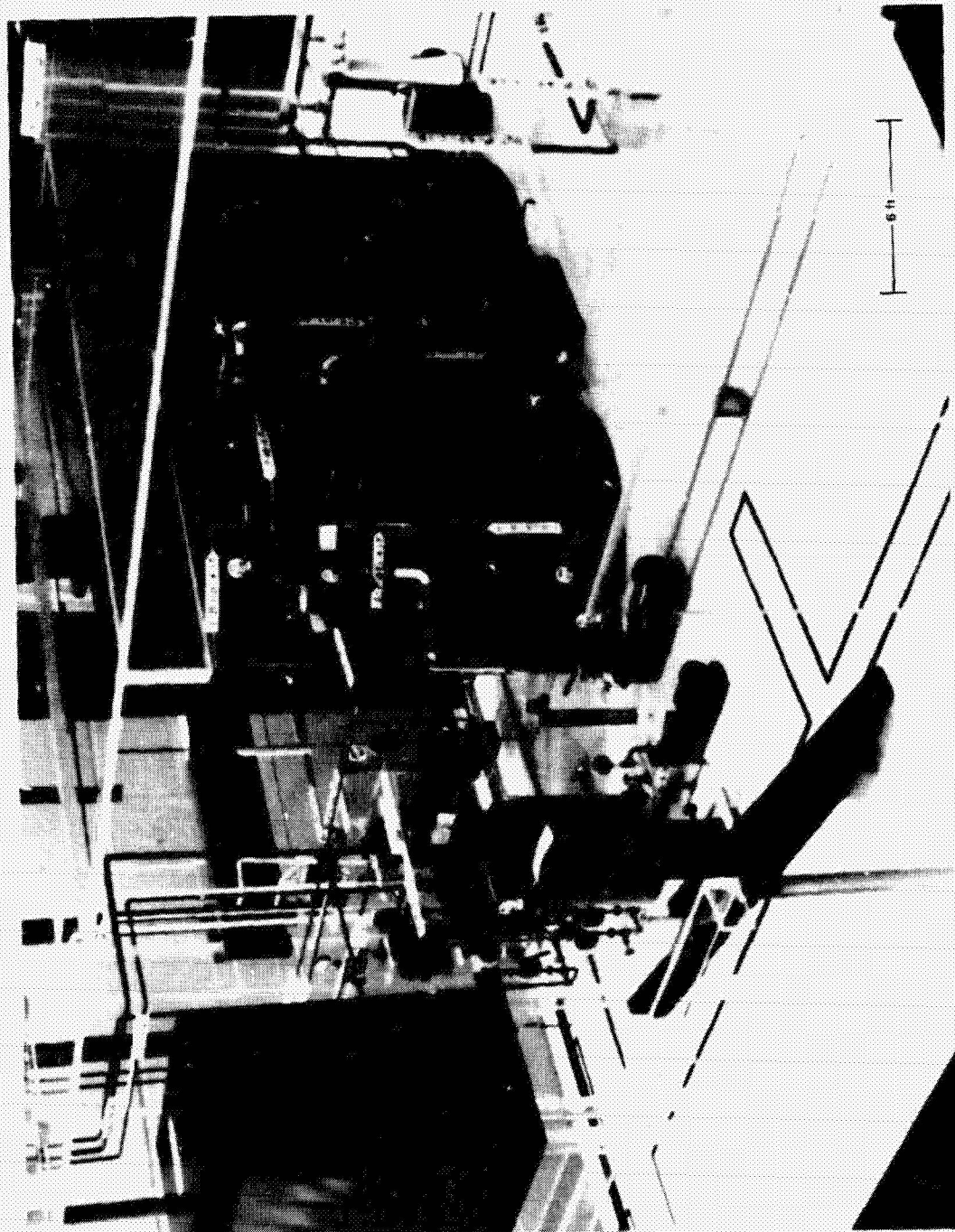


FIGURE 7. WASTE DISPOSAL AREA

The large tank in the center is the vent gas scrubber with the equipment for neutralizing chlorine and  $\text{SiCl}_4$  shown on the left. The large tank at the right rear is for the storage of sodium hypochlorite formed by the chlorine neutralization. The power supply for the electrolytic cells is shown at the extreme left. Scale = 1/75

With this design as a basis, detailed estimates were made of the cost of installing the EPSDU in an existing building at Battelle Columbus Laboratories. Estimates made by RKAI in cooperation with BCL staff, as well as by an independent process design group at BCL, ranged from \$1.5 to \$1.6 million, as discussed in greater detail in the Eleventh/Twelfth Quarterly Report(3).

Although the decision was made to adopt the PDU program instead of constructing the EPSDU immediately, the EPSDU design remains valid as a basis for future scale-up, subject, of course, to modifications as indicated by the PDU experience described in this report.

ECONOMIC ANALYSIS OF SILICON PRODUCTION AT THE  
1000 MT/YEAR LEVEL

Toward the end of the program covered in the Phase I/II Final Report<sup>(1)</sup>, an update of an earlier 1000 MT/year economic analysis was made based on the 50 MT/year EPSDU design then current. Although changes have been made in the EPSDU design in the early part of Phase III, it is believed that the effect on the economic analysis would not be sufficient to warrant recalculation of the estimates. Accordingly, this has not been done.

It is of interest here, however, to bring those figures up to date in terms of using 1980 dollars in place of 1975 dollars, and providing for return on investment, which was not done in the earlier calculations. In accomplishing this update, the 1975-based figures are multiplied by the inflation factor 1.4. Further, the selling price of the product on the basis of return on investment (R.O.I.) is calculated by the formula:

$$P = C + \frac{1.15 FR}{1-T} \quad (1)$$

where P = selling price, \$/kg

C = product cost without profit, \$/kg

F = fixed capital investment, \$/kg

R = return on investment, %/100

T = tax rate, %/100

1.15 = factor allowing for working capital = 15% of fixed capital

Table 1 gives the projected selling price as a function of ROI for silicon produced by the zinc reduction process in accordance with the options studied earlier.

As shown in Table 1, both Cases II and III meet a product cost goal of <\$14/kg (1980 dollars). However, to achieve a reasonable return on investment requires a mark-up of, e.g., approximately 50 percent for a 20 percent R.O.I., so that a correspondingly lower product cost is necessary to reach a selling price goal of <\$14/kg (1980 dollars).

TABLE 1. SELLING PRICE OF SILICON FOR VARIOUS LEVELS OF  
RETURN ON INVESTMENT, 1000 MT/YEAR, UNIT = 1 kg,  
FEDERAL TAX RATE = 46 PERCENT; BASIS: DATA  
FROM PHASE I/II FINAL REPORT(1).

CASE	I	II	III
BASIS	Six 43-cm-dia Fluidized-Bed Reactors Twelve 60,000-amp Electrolytic Cells	Two 74-cm-dia Fluidized-Bed Reactors Twelve 60,000-amp Electrolytic Cells	One 104-cm-dia Fluidized-Bed Reactor One 7,200,000-Amp Equi- valent Electrolytic Cell
Fixed Capital (\$1975)	\$15.48	\$10.72	\$7.57
Fixed Capital (\$1980)	21.67	15.01	10.60
Product Cost (\$1975)	11.21	8.71	7.35
Product Cost (\$1980)	15.69	12.19	10.29
Product Selling Price (\$1980)			
0% R.O.I.	15.69	12.19	10.29
10% R.O.I.	20.30	15.39	12.55
15% R.O.I.	22.61	16.98	13.68
20% R.O.I.	24.92	18.58	14.80
25% R.O.I.	27.23	20.18	15.93
30% R.O.I.	29.53	21.78	17.06

### ENERGY PAY-BACK

As recorded in the Phase I/II Final Report<sup>(1)</sup>, solar photovoltaic cells of 10 percent efficiency would require an elapsed time (night and day) of 5.9 months to replace the energy consumed in the production of the silicon by the zinc reduction process. That calculation was based on the projected use of metallurgical-grade silicon for the production of silicon tetrachloride. However, several advantages of using silicon carbide in place of metallurgical-grade silicon have come to light, not the least of which is a considerable saving in energy consumption.

Most of the direct\* producers of silicon tetrachloride use silicon carbide as a silicon source because of a cost advantage over the use of metallurgical-grade silicon and because the reaction with chlorine is less exothermic. Thus it is probable that a 1000 MT/year plant would be designed accordingly. The use of silicon carbide in the energy calculations is also more consistent with the prior cost calculations which were based on a selling price of silicon tetrachloride produced from silicon carbide.

In making the revised energy use calculations, an additional amount of power, largely due to refrigeration costs, is added for the manufacture of silicon tetrachloride.

From Table 27 of the Phase I/II Final Report<sup>(1)</sup>, we note that the process requires 15.68 lb of SiCl<sub>4</sub> per kg of silicon. At 0.30 kWh/lb of SiCl<sub>4</sub>\*\*, that amounts to 4.70 kWh/kg Si. The energy requirement for the production of silicon carbide (87 percent SiC\*\*\*) is 2.5 kWh/lb\*\*\*\*. Thus if the SiC is converted to SiCl<sub>4</sub> at a utilization efficiency of 95 percent, the energy required due to the SiC is

$$(2.5 \div 0.87) \times \frac{40.09 \text{ (mol wt SiC)}}{169.93 \text{ (mol wt SiCl}_4\text{)}} \times (15.68 \div 0.95) = 11.2 \text{ kWh/kg Si.}$$

---

\* Much SiCl<sub>4</sub> is a byproduct of other operations.

\*\* Estimate from producer of SiCl<sub>4</sub>; identity withheld.

\*\*\* Some of the SiO<sub>2</sub> + C in the 13 percent non-SiC content of the silicon carbide product will chlorinate. However, the conservative position of neglecting this is taken here.

\*\*\*\* Estimate from producer of SiC; identity withheld.

Table 2 presents a revision of Table 31 of the Phase I/II Final Report<sup>(1)</sup> to account for the use of SiC, rather than metallurgical-grade silicon, in the production of SiCl<sub>4</sub>. In addition, it accounts for a more realistic energy consumption in the SiCl<sub>4</sub> production step. The total of 56.72 kWh/kg Si based on the use of SiC for the preparation of the SiCl<sub>4</sub> compares with 71.27 kWh/kg Si obtained earlier with metallurgical-grade silicon as the starting material. The saving is due mainly to the high energy utilization efficiency of the Acheson furnace for silicon carbide production relative to that of the arc furnace used to produce metallurgical-grade silicon.

To calculate the time necessary to pay back the energy consumed in the manufacture of the silicon, one can assume a solar cell 0.0254 cm in thickness generating a peak power of 100 watts per square meter. In an area where the average power is 20 percent of the peak power and with an assumption of 50 percent loss of silicon in the cell manufacture, the average power output per kg of silicon produced by the process is

$$\frac{100 \times 0.20 \times 0.50}{0.0254 \times 100^2 \times 2.3} = 0.0171 \text{ watts/g or } 0.017 \text{ kW/kg,}$$

where 2.3 g cm<sup>-3</sup> is the density of silicon. On this basis, 56.72/0.0171 = 3314 hours, or 4.5 months, would be required for the energy pay-back.

TABLE 2. ENERGY REQUIREMENTS, kwh/kg Si.

Item	Basis	Energy Requirement kwh/kg Si	
		This Report	Reference (1)
Process, with Exception of SiCl <sub>4</sub> Production	Table 28, Reference 1	36.46	36.46
SiCl <sub>4</sub> Production	See Text	4.70	---
Make-up Cl <sub>2</sub>	2.04 lb/kg Si @ 1.54 kWh/lb <sup>(a)</sup>	--- <sup>(b)</sup>	--- <sup>(b)</sup>
NaOH to Neutralize Waste SiCl <sub>4</sub>	2.4 lb/kg Si @ 1.37 kWh/lb <sup>(a)</sup> 97 Percent Utilization	3.29	3.29
Make-up Zinc	0.54 lb/kg Si @ 2 kWh/lb <sup>(c)</sup>	1.08	1.08
Silicon Carbide	See Text	11.19	---
Metallurgical-Grade Silicon	1.27 lb/kg Si @ 24 kWh/kg 95 Percent Utilization	---	30.44
TOTAL		56.72	71.27

(a) See Reference 5.

(b) Co-product of NaOH production.

(c) Conservative estimate of 2 kWh/lb Zn adopted on basis of 1.6 kWh/lb projected by U. S. Bureau of Mines, Reno, Nevada<sup>(6)</sup>.

### PROCESS DEVELOPMENT UNIT (PDU)

As noted in the Introduction to this report, a decision was made not to proceed immediately with construction of the EPSDU, but to determine the operability of the four most critical units of that design on the basis of an 8-hour batch operation. This required the construction of those units and assembling the items of auxiliary equipment that were necessary for such an operation. The overall experimental facility was termed the Process Development Unit (PDU).

This facility included a 7-inch-diameter fluidized bed of 25 MT/year capacity\*, a  $\text{Zn/ZnCl}_2$  by-product condenser of the same capacity, and a 6,000-amp electrolytic cell for recovery of zinc and chlorine values from the by-product zinc chloride. The electrolytic cell is one of six in the EPSDU design. A suitable holding tank was provided to accommodate the by-product and to permit operation of the electrolytic cell and fluidized bed independently. The other critical unit of the EPSDU incorporated in the PDU was the zinc vaporizer, characterized by direct inductive coupling to the zinc in a vaporizer of minimal thermal capacity to avoid hysteresis in the rate of generation of zinc vapor.

Figure 8 (a-c) is a schematic diagram of the PDU, showing the critical units mentioned above and the auxiliary equipment.

Figure 9 shows a general view of the PDU. The operator is kneeling at the top of the fluidized-bed reactor furnace. Behind and to his left, extending to the ceiling, is the  $\text{Zn/ZnCl}_2$  by-product condenser. The  $\text{SiCl}_4$  vaporizer is seen to the left of the reactor furnace at floor level, and part of the electrolytic cell extends to the right of the frame at floor level. The cable tray, making a 90-degree bend in the lower foreground, carries the connections from instrumentation to the control panel.

Figure 10 is a schematic diagram of the fluidized-bed reactor from the EPSDU design. For use in the PDU, the seed inlet was omitted, since it was unnecessary to add seed during the eight hours of operation. Charging of

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\* One of the two 25-MT/year reactors of the 50-MT/year EPSDU design.

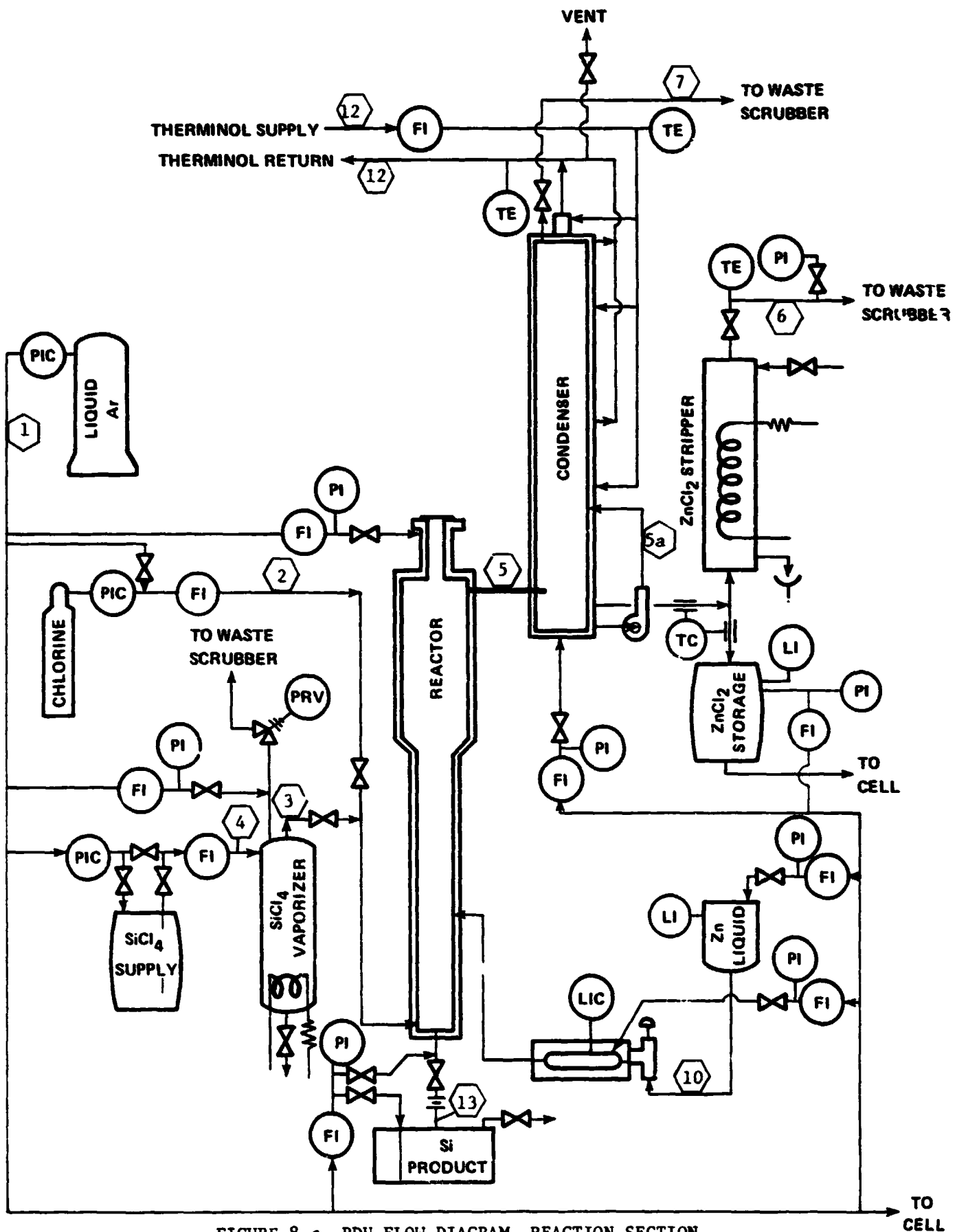


FIGURE 8 a. PDU FLOW DIAGRAM, REACTION SECTION

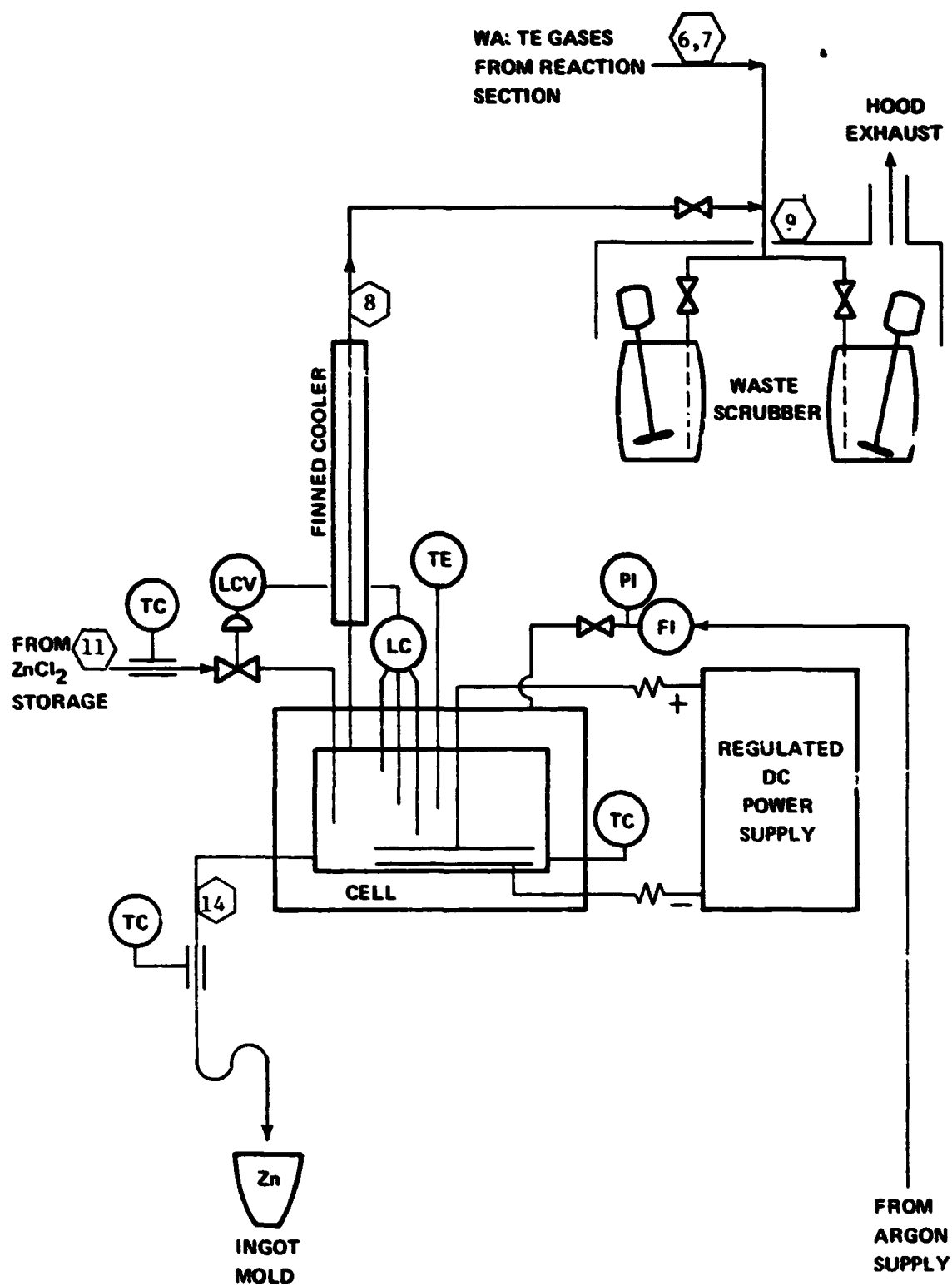


FIGURE 8 b. PDU FLOW DIAGRAM, REACTION-PRODUCT TREATMENT SECTION

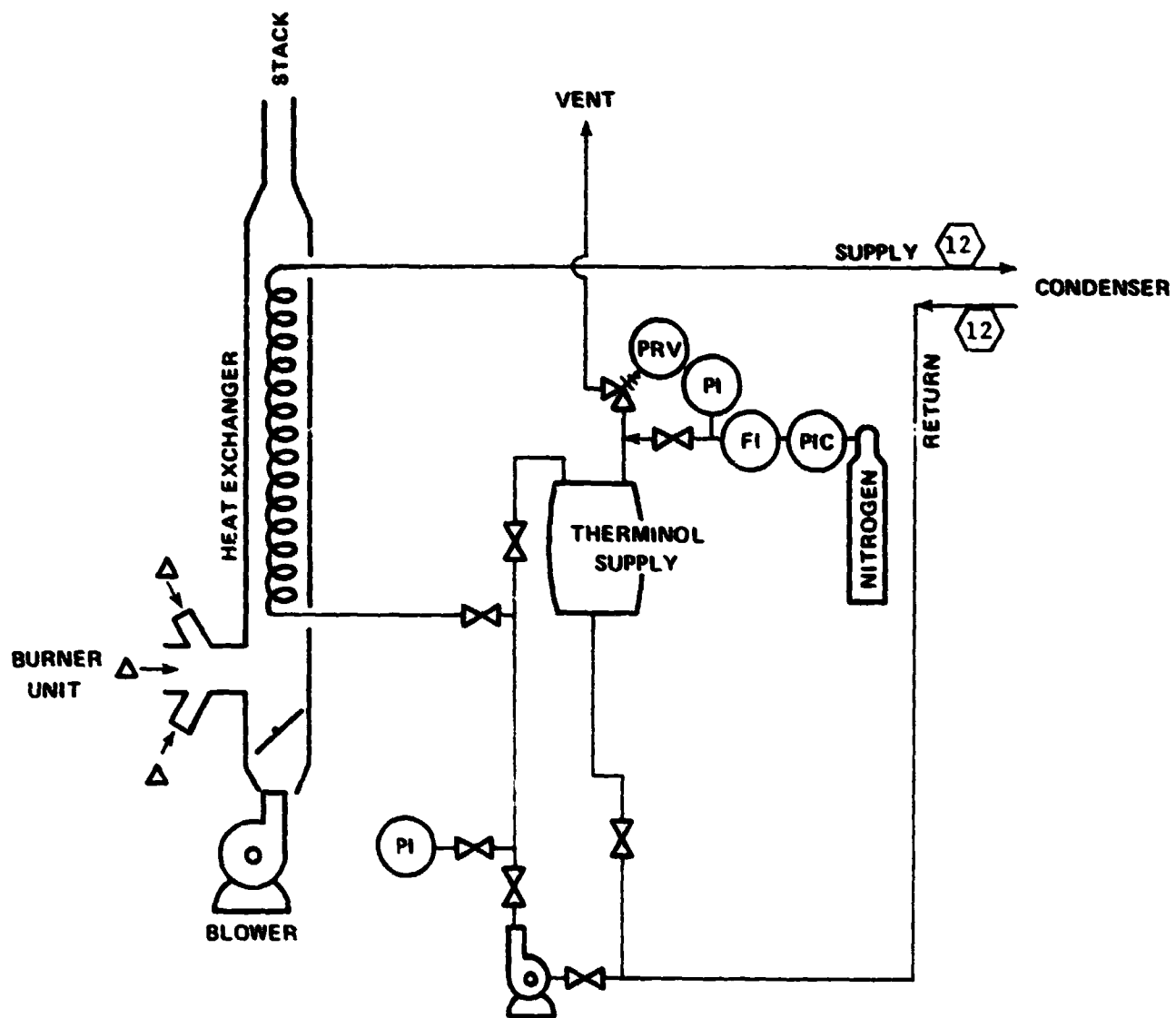


FIGURE 8 c. PDU FLOW DIAGRAM, HEAT-TRANSFER SYSTEM

# FIGURE 8 ADDENDUM

## NOMINAL PDU PROCESS STREAM COMPOSITION AND RATES

1. Argon, cumulative
2.  $\text{Cl}_2(\text{g})$ , 1.5 lb/hr (average of intermittent use\*)
3.  $\text{SiCl}_4(\text{g})$ , 80.0 lb/hr
4.  $\text{SiCl}_4(\text{l})$ , 80.0 lb/hr
5.  $\text{ZnCl}_2(\text{l})$ ,  $(80.9-x)\text{lb/hr}^{**}$                        $\text{Zn}(\text{s})$ , 22.8 lb/hr  
 $\text{ZnCl}_2(\text{s})$ , x lb/hr                                       $\text{Si}(\text{s})$ , 0.16 lb/hr  
 $\text{SiCl}_4(\text{g})$ , 29.6 lb/hr                                       $\text{Ar}(\text{g})$ , 10.9 scfh
- 5a.  $\text{ZnCl}_2(\text{l})$ , 2.4 gal/min
6.  $\text{SiCl}_4(\text{g})$ , 29.6 lb/hr  
 $\text{Ar}(\text{g})$ , 10.9 scfh
7.  $\text{SiCl}_4(\text{g})$ , 1.4 lb/hr (average of intermittent use)  
 $\text{Cl}_2(\text{g})$ , 0.3 lb/hr (average of intermittent use)
8.  $\text{Cl}_2(\text{g})$ , 41.3 lb/hr (average of intermittent use)  
 $\text{SiCl}_4(\text{g})$ , 1.0 lb/hr (average of intermittent use)
9.  $\text{SiCl}_4(\text{g})$ , 32.0 lb/hr (average of intermittent use)  
 $\text{Cl}_2(\text{g})$ , 41.3 lb/hr (average of intermittent use)  
 $\text{Ar}(\text{g})$ , 10.9 scfh (average of intermittent use)
10.  $\text{Zn}(\text{l})$ , 61.6 lb/hr
11.  $\text{ZnCl}_2(\text{l})$ , 80.9 lb/hr (average of intermittent use)  
 $\text{Zn}(\text{s})$ , 22.8 lb/hr (average of intermittent use)  
 $\text{Si}(\text{s})$ , 0.16 lb/hr (average of intermittent use)
12. Therminol coolant, 11 gpm
13. Silicon product, 7.9 lb/hr + seed content
14.  $\text{Zn}(\text{l})$ , 61.6 lb/hr (average of intermittent use)

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\* Averaged over time of operation of fluidized bed; actual rate =  $K \times$  recorded rate, where

$$K = \frac{\text{operating time of fluidized bed}}{\text{operating time of chlorination or electrolysis}}$$

\*\* x = small amount (e.g., <1 percent) of uncondensed  $\text{ZnCl}_2$ .

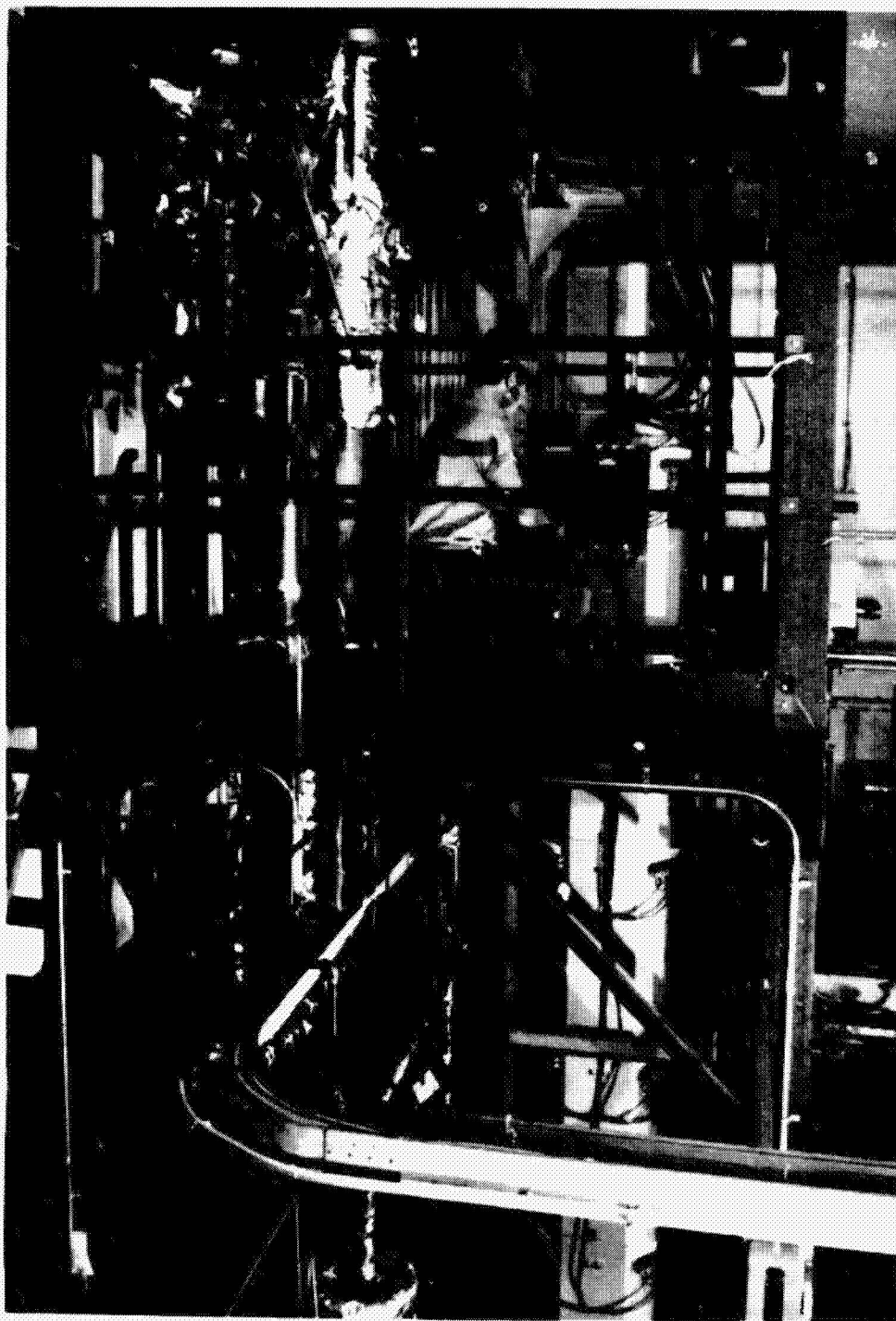


FIGURE 9. PROCESS DEVELOPMENT UNIT (PDU)

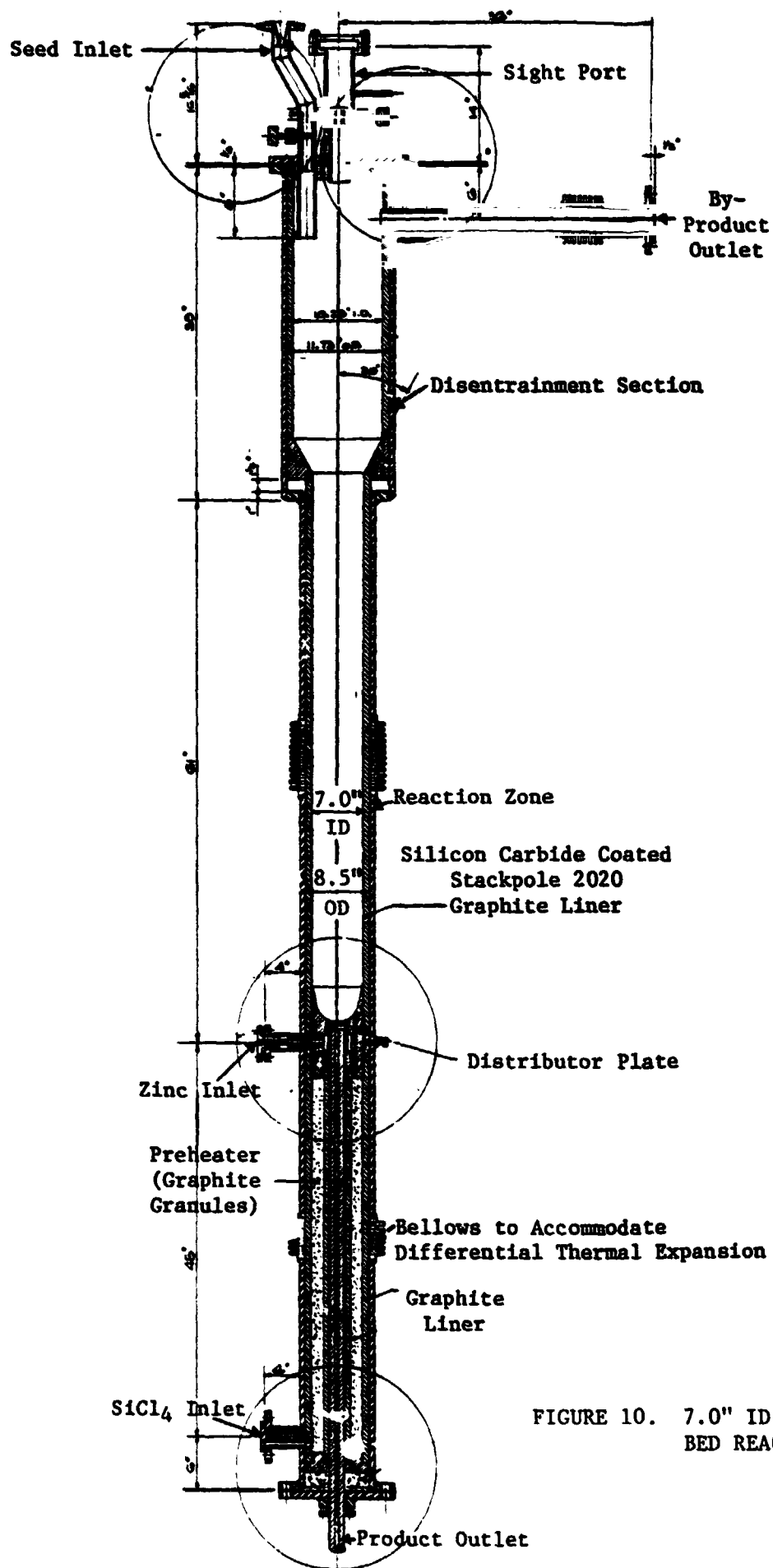


FIGURE 10. 7.0" ID FLUIDIZED BED REACTOR

the starting bed to the reactor was done through the sight port, which resumed its normal function during operation.

The reactor itself was constructed of Stackpole 2020\* graphite and was sealed on the outside with UCAR-14 resin (UCC). After the resin was cured, the inside of the reactor was coated\*\* with silicon/silicon carbide\*\*\* by thermal decomposition of trichlorosilane, about 10 percent in argon, introduced through alternate inlets. The temperature was purposely kept low (700-750 C) so that the fraction of trichlorosilane that reacted was limited to <5 percent. In this way, the coating reaction was spread over the entire inner surface of the reactor. Test coupons of graphite placed strategically in the reactor received continuous<sup>†</sup> coatings of silicon, ranging from 1/ $\mu$ m to 4/ $\mu$ m thickness, depending on location. The purpose of the coatings was (1) to minimize the permeability of the graphite to zinc and zinc chloride vapors which are deleterious to the stainless steel reactor shell, and (2) to minimize transport of impurities from the reactor to the reaction zone.

The zinc vaporizer design first used, and in principal the preferred design, is shown in Figure 11. The direct-coupled vaporizer design was adopted because the technology is not available for controlling and monitoring the flow of zinc vapor at atmospheric pressure and a little above at the required temperatures of 908 to 920 C.

Because of the high heat of vaporization of zinc, (27.6 kcal/mole, as contrasted with water, 9.8), it should be possible to control the rate of zinc vapor feed to the reactor by the power input to the vaporizer. This is best done with a minimum of hysteresis in the control by minimizing the thermal capacity of the vaporizer, i.e., by coupling electromagnetic energy directly to the zinc. It should also be possible in principal to monitor the zinc inventory in the vaporizer by the coupling characteristics.

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\* Stackpole Carbon Co.

\*\* Including the internal surface of the SiCl<sub>4</sub> preheater and the inlets and outlets.

\*\*\* The SiC would be limited to a superficial reaction layer at the interface.

† Except at deep pores.

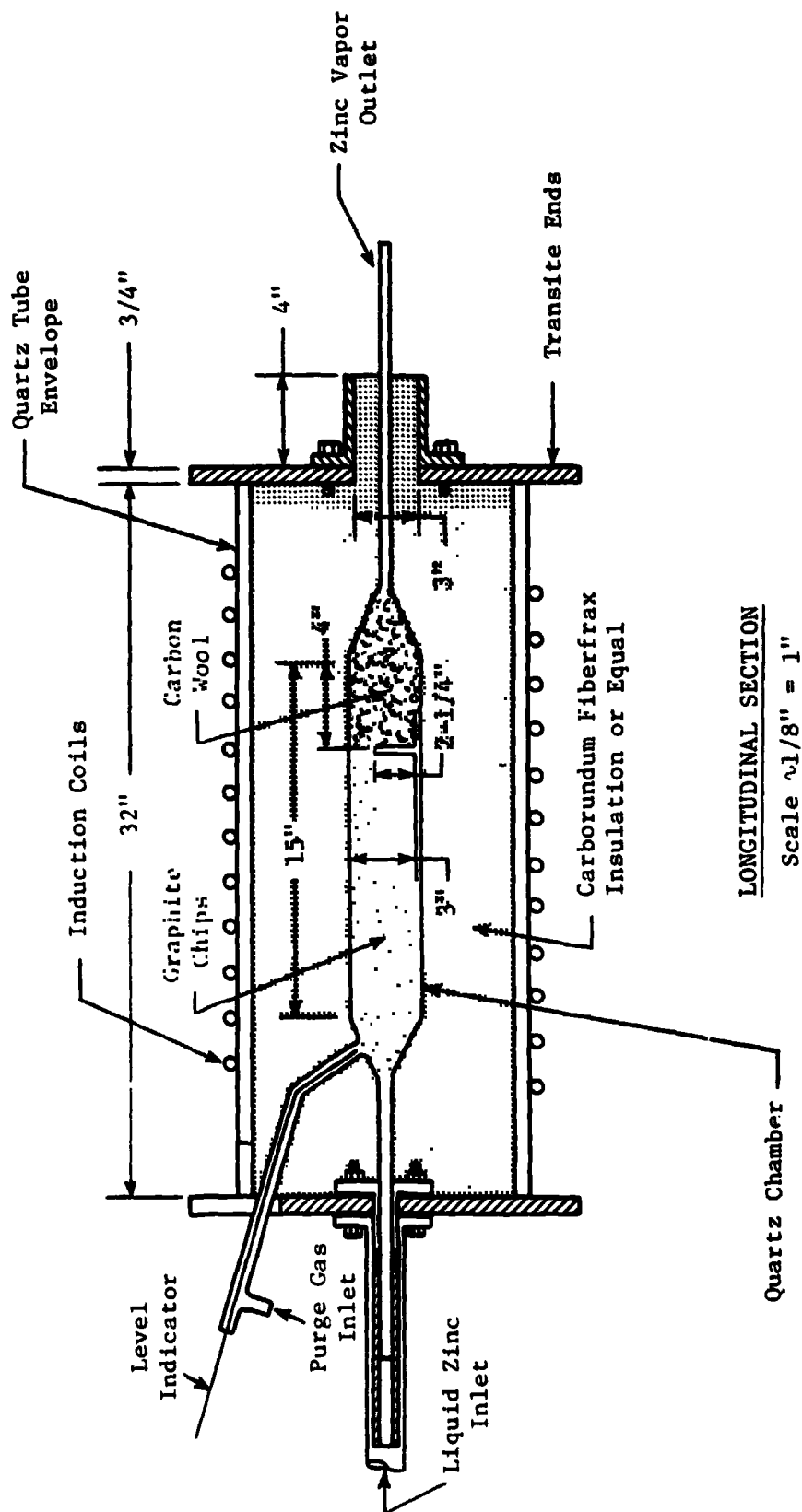


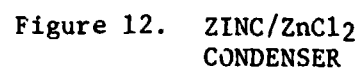
FIGURE 11. ZINC VAPORIZER

Because of arcing problems related to the wave form of the particular electromagnetic generator that was available for this work, an alternative vaporizer had to be substituted, as described in the section of this report dealing with PDU experience.

The Zn/ZnCl<sub>2</sub> condenser of the PDU is shown as two cross sections at right angles in Figure 12. Vapors from the reactor containing unreacted zinc and silicon tetrachloride plus by-product zinc chloride and the argon "breather" gas enter from the bottom left of the left-hand cross-section view. The pass partition, extending below the liquid ZnCl<sub>2</sub> level at the bottom, directs the vapors up the open tubes on the left (only one of three parallel tubes is shown) and then down on the right. These channels are wetted with a film of recirculated ZnCl<sub>2</sub>, which is pumped to a distributor/overflow section at the top of the condenser through the parallel tubes shown in the right cross section. The purposes of the wetted wall at 350 C are to improve the condensation of the zinc chloride, to permit the condensation of zinc as a fine particulate solid, and to collect entrained finely divided silicon for transport to the electrolytic cell where it is chlorinated.

The by-product condenser shown in Figure 12 differs from that shown as Figure 24 in the Phase I/II Final Report<sup>(1)</sup> by the elimination of the flow of Therminol heat-exchange fluid within the graphite block and the substitution of flow through a plate-coil jacket on the outside stainless steel wall and a bayonet cooler extending as a well into the center of the condenser. Although the heat transfer is not as good as in the original design, it was thought to be adequate, and the construction of the condenser is greatly simplified. Further, the potential for leakage of the Therminol heat-exchange fluid into the process stream is greatly reduced.

The electrolytic cell of the PDU shown in Figure 13 is one of the six 6000-amp cells of the 50 MT/year EPSDU design. Accordingly, 8-hour operation of the 25 MT/year-equivalent reactor of the PDU requires 24 hours operation of the electrolytic cell to handle the zinc chloride by-product. The electrolytic cell is patterned after those being developed at the U. S. Bureau of Mines at Reno, Nevada<sup>(7)</sup>, <sup>(8)</sup> for the electrolysis of zinc chloride. The electrolyte is a 50/50 m/o mixture of KCl and ZnCl<sub>2</sub>, the KCl addition being for the purpose of increasing the cell conductivity and decreasing the vapor pressure of the ZnCl<sub>2</sub>(g) over the electrolyte<sup>(7)</sup>. The KCl is retained



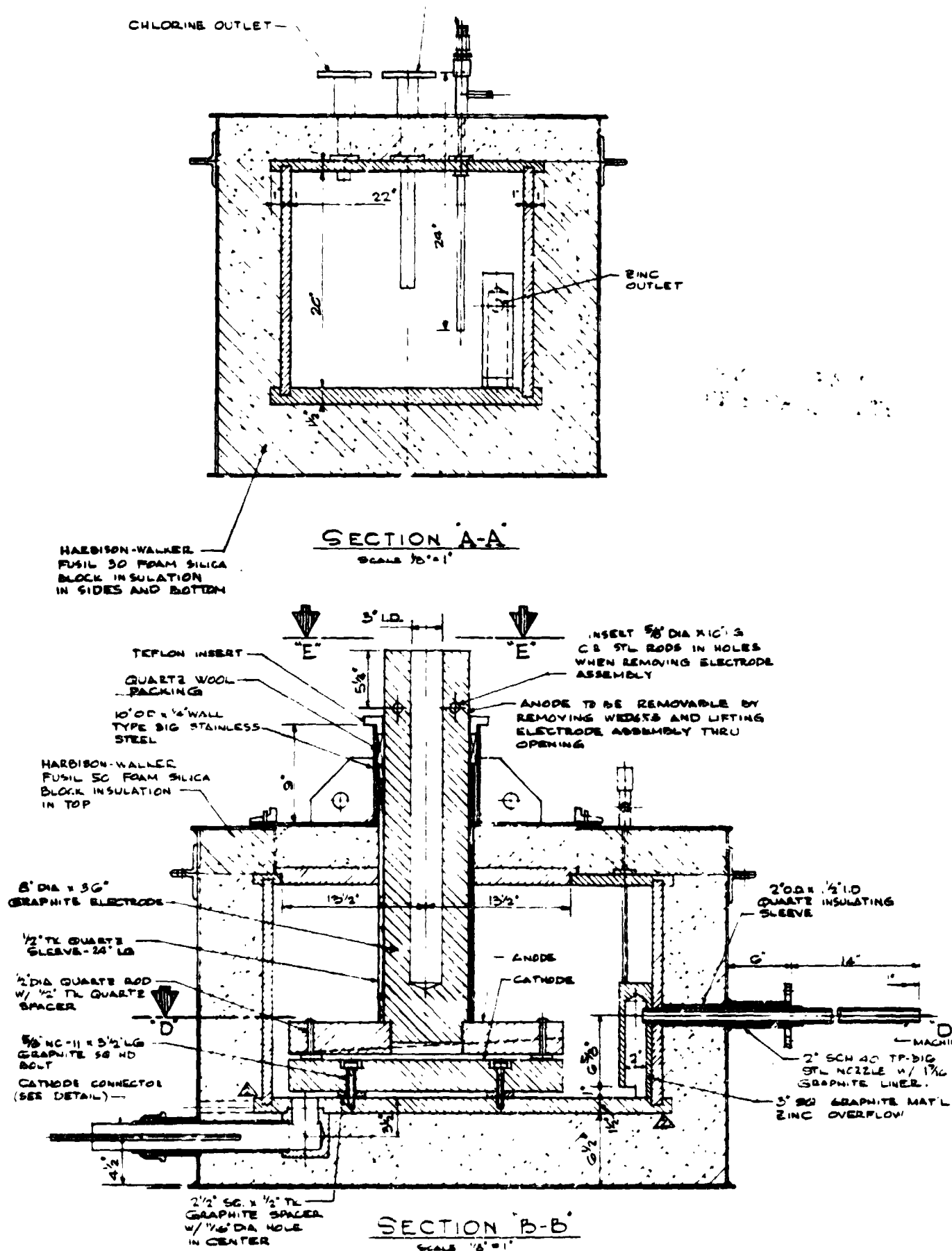


FIGURE 13. ELECTROLYTIC CELL

in the cell, which with periodic additions of  $\text{ZnCl}_2$  (+ Zn) from the storage tank is operated in the range from ~45 m/o to ~55 m/o  $\text{ZnCl}_2$ . A significant difference between the BCL and USBM cells is that, whereas the zinc product is withdrawn from the latter by means of an evacuated dip tube, the BCL cell provides for discharge of zinc by overflow through a siphon on the side wall. The  $\text{ZnCl}_2$  level in the cell is monitored between limits by a level probe extending from the ceiling of the cell. In normal operation the hydrostatic head of the  $\text{ZnCl}_2$  (density =  $2.5 \text{ gcm}^{-3}$ ) floating on the zinc (density =  $6 \text{ gcm}^{-3}$ ) within the cell balances the head of zinc in the overflow. At a constant head ( $h_o$ ) of zinc in the overflow, the zinc level in the cell ( $h_z$ ) is directly determined by the  $\text{ZnCl}_2$  level ( $h_c$ ) as:

$$(h_c - h_z) = \frac{6.6}{2.5} (h_o - h_z).$$

If the level of  $\text{ZnCl}_2$  is maintained by periodic addition of  $\text{ZnCl}_2$ , the zinc level inside the cell is maintained by overflow of zinc as it is generated by electrolysis of the  $\text{ZnCl}_2$ .

In addition to the four critical units of the PDU discussed above, several items of auxiliary equipment are shown in Figure 8, which are essential to the 8-hour batch operation of the PDU. These include:

- (1)  $\text{SiCl}_4$  supply tank, stainless steel, 55-gal, 689 lb, 8.6 hr supply at nominal (Figure 8) rate.
- (2)  $\text{Cl}_2$  supply, for intermittent chlorination of silicon deposited on walls of reactor.
- (3) Argon supply, 160 l of liquid argon as purge/breather gas.
- (4) Silicon product storage hopper, stainless steel, capacity 7 gal, for use in withdrawing the product and starting bed from the reactor, i.e., to confirm the concept of periodic product withdrawal.
- (5)  $\text{ZnCl}_2$  storage tank, stainless steel, 55 gal, for interim storage of by-product containing mainly  $\text{ZnCl}_2$  plus unreacted Zn and entrained finely divided silicon.

- (6) A zinc storage tank, graphite lined, capacity 10 gal = 550 lb of zinc.
- (7) Ingot molds for casting the zinc produced by the electrolytic cell.
- (8) A  $\text{ZnCl}_2$  stripper consisting of a water-cooled vertical finned tube to remove  $\text{ZnCl}_2$  that escapes the  $\text{Zn}/\text{ZnCl}_2$  by-product condenser, so as to prevent plugging of the downstream lines (stripper heated periodically to melt down condensate).
- (9) Neutralization tanks, stainless steel, 55 gal, for use in neutralizing residual  $\text{SiCl}_4$  and chlorine with calcium hydroxide.
- (10) A gas-fired, air-cooled, Therminol-66\* system for removing the heat of condensation and sensible heat from the by-product gases.

Although the major objective of the PDU program was to demonstrate the operability of the four critical EPSDU units and to collect engineering data, an effort was made to obtain as high a purity as possible in the silicon product so that it might be useful within the LSA Project. To that end, high-purity semiconductor-grade silicon was obtained and crushed and leached for use as seed particles, as described in the Phase I/II Final Report<sup>(1)</sup>. Further, semiconductor-grade  $\text{SiCl}_4$ \*\* was used in conjunction with high-purity zinc\*\*\*. The initial coating of the reactor with silicon was designed to minimize impurity transfer from the graphite, as noted previously.

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\* Monsanto Company.

\*\* Semiconductor-grade  $\text{SiCl}_4$ , Texas Instruments, Inc.

\*\*\* 99.99 percent, Belmont Smelting & Refining Works, Inc.

### PDU OPERATION

Operation of the PDU was designed to answer the following questions:

- (1) Will the  $\text{SiCl}_4(\text{g})$  preheater (lower section of the fluidized-bed reactor) perform as designed? What is the available margin?
- (2) Can adequate control of the vaporization rate of zinc be exercised via induction heater power control?
- (3) Can the zinc inventory in the vaporizer be monitored by its inductive characteristics?
- (4) Can zinc vapor free of zinc mist be generated\*?
- (5) Are the fluidization characteristics, shown to be satisfactory in the Miniplant and in room-temperature modelling experiments, reproduced in the PDU reactor?
- (6) Are the favorably high reaction efficiency ( $\sim 60$  percent) and silicon production rate ( $\sim 30 \text{ lb/hr ft}^2$ ) maintained in the larger reactor?
- (7) Can the negative temperature gradient toward the top of the fluidized-bed reactor be maintained in the larger unit so that appreciably increased reaction efficiency can be gained as was observed in the Miniplant?
- (8) Are the amounts of silicon wall deposit, gas-phase-nucleated silicon and entrained zinc chloride within the manageable limits predicted from Miniplant experience?
- (9) What rate of chlorination of the silicon wall deposit can be maintained at reasonable chlorine utilization efficiency?
- (10) Does the time required for chlorination fit into a reasonable turn-around cycle?

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\* It is essential that the amount of zinc mist entering the reactor be minimized, as it is known to lead to the formation of fine silicon needles.

- (11) Can the proper gas purge and silicon granule flow balance be maintained in the product-withdrawal tube so as to prevent condensation of zinc in the withdrawal tube?
- (12) Can undesirable segregation of the finely divided Zn(s) and Si(s) be avoided before the 350 C slurry reaches the electrolytic cell at 500 C (melting point of zinc = 420 C)?
- (13) Can the condensed by-product slurry containing finely divided Zn(s) (~9 v/o) and Si(s) (~0.2 v/o) be recirculated in the condenser so as to provide the wetted-wall action required for operation of the condenser as designed?
- (14) Can acceptable current and power efficiencies be maintained in the electrolytic cell despite the potential restriction of electrolyte flow resulting from increasing the anode area by 2.5 times that currently used at the Bureau of Mines, Reno Station? (Although the anode area is increased by 2.5 times, the length of the channel through which the electrolyte circulates is increased by a factor of only 1.4.)
- (15) Are there unforeseen problems with the critical equipment items or with other parts of the PDU whose early solution would benefit a subsequent EPSDU program?

PDU activities will be discussed in terms of (1) a description of a normal start-up and operating procedure, (2) a history of actual operating experience, and (3) a discussion, based on that operating experience, of the operability of the four basic units being evaluated in the PDU.

### PDU Start-up and Operating Procedure

Normal operation of the PDU called for maintaining the fluidized bed and its associated equipment at temperature at all times, and initiating and terminating the runs by feeding reactants and collecting reaction products in batches corresponding to the feeding of 650 lb of  $\text{SiCl}_4$  (63.2 lb of silicon product in 8-hour operation under conditions of Figure 10).

The electrolytic cell, being one-third the capacity of the three in the 25 MT/year EPSDU design, would be operated between PDU runs three hours for every one hour of PDU operation.

The importance of keeping the reactor system hot was to avoid the problem of differential contraction once the system had been successfully brought to operating temperature.

Although the operating procedure (including bringing the system to operating temperature) was altered during the course of the program as the result of experience, it may be described in its preferred form as shown in Table 3.

TABLE 3. PDU PROCEDURES.

Operation No.	Operation
<u>START-UP PROCEDURE</u>	
1	<p>Fill zinc reservoir with anode balls and/or electrolytic cell product and start argon purge to melter, transfer piping and valve.</p> <p>Note: If melter is already hot and zinc molten, addition of zinc melt stock must be done very carefully to avoid possible damage to cement joint at outlet tube.</p>
2	Heat zinc reservoir, piping and valve to 450 - 500 C, allowing sufficient time for entire charge to become molten.
3	<p>Start argon purge flows to remaining system components:</p> <p>Zinc vaporizer and feeder @ ~400 cc/min  <math>\text{SiCl}_4</math> vaporizer @ ~400 cc/min  Reactor discharge port @ ~500 cc/min  Reactor top shell @ minimum detectable flow to keep manometer pressure equal or greater than that of reactor freeboard manometer  Reactor bottom shell @ ~600 cc/min  Reactor sight port @ ~500 cc/min  Reactor/condenser flange connection @ ~500 cc/min  Condenser shell top @ ~350 cc/min  Condenser sump, packing gland, flange connections @ low but positive flows  <math>\text{ZnCl}_2</math> reservoir @ ~350 cc/min  <math>\text{ZnCl}_2</math> auxiliary feed tank @ ~350 cc/min</p>
4	Begin heat-up of system components.
4.1	<p>Reactor Heaters: Zone 1 to 950 C  Zone 2 to 950 C  Zone 3 to 950 C  Zone 4 to 900-910 C  Zone 5 to 875-890 C</p> <p>Note: During reactor heating, reactor/condenser flange connection must be controlled to permit graphite flanges to move laterally without restraint. <math>\text{SiCl}_4</math> inlet flange bolts should be removed, bolt holes sealed, and flange periphery sealed with neoprene band.</p>

TABLE 3. CONTINUED.

Operation No.	Operation														
4.1	Note, Cont: A solid graphite disc spacer is inserted in reactor/condenser connection until both reactor and condenser are fully heated. Disc then replaced with graphite ring and connection tightened.														
4.2	Condenser system: Condenser bottom (2 zone) to 350-360 C Condenser sump to 350 C Condenser/sump and condenser outlet connections to 350 C Auxilliary $\text{ZnCl}_2$ tank to 350 C Therminol system to 350-355 C Condenser top heater to 365-380 C  Note: Internal temperature at top of condenser must be to 330 C before starting run.  Condenser liquid discharge piping and $\text{ZnCl}_2$ storage tank to 350 C Vapor discharge piping to 350 C														
4.3	$\text{SiCl}_4$ vaporizer to 175-200 C $\text{SiCl}_4$ vapor piping to 200 C														
5	After reactor has achieved operating temperature, carefully tighten $\text{SiCl}_4$ inlet, reactor/condenser flange connections, place atmosphere purge band on reactor/condenser connection														
6	Insulate reactor/condenser piping and heat to 900 C.														
7	Adjust $\text{ZnCl}_2$ level in condenser reservoir and sump tank.														
8	Prepare exhaust gas neutralizer drums; 20-30 lb (9-14 kg) lime to 40 gal $\text{H}_2\text{O}$ and indicator.														
9	Check all valves in system for proper position: <table> <tr> <td>Chlorination inlet</td><td>Closed</td></tr> <tr> <td>Chlorination exhaust</td><td>Closed</td></tr> <tr> <td>Stripper vapor exhaust</td><td>Open</td></tr> <tr> <td><math>\text{ZnCl}_2</math> reservoir inlet</td><td>Open</td></tr> <tr> <td><math>\text{ZnCl}_2</math> reservoir drain</td><td>Closed</td></tr> <tr> <td>Cell <math>\text{Cl}_2</math> exhaust</td><td>Closed</td></tr> <tr> <td>Condenser equalizer</td><td>Open</td></tr> </table>	Chlorination inlet	Closed	Chlorination exhaust	Closed	Stripper vapor exhaust	Open	$\text{ZnCl}_2$ reservoir inlet	Open	$\text{ZnCl}_2$ reservoir drain	Closed	Cell $\text{Cl}_2$ exhaust	Closed	Condenser equalizer	Open
Chlorination inlet	Closed														
Chlorination exhaust	Closed														
Stripper vapor exhaust	Open														
$\text{ZnCl}_2$ reservoir inlet	Open														
$\text{ZnCl}_2$ reservoir drain	Closed														
Cell $\text{Cl}_2$ exhaust	Closed														
Condenser equalizer	Open														

TABLE 3. CONTINUED.

Operation No.	Operation
9	Exhaust liquid trap inlet and outlet      Open Exhaust liquid trap by-pass                  Closed Exhaust gas scrubber (2)                      1 Open, 1 Closed Silicon product drain flapper                Closed Sight port flapper                              Closed
10	Check system for gas tightness, continuity of flow paths through system and possibility of blockage by increasing individual purge flows, observing bubbling at neutralizers and observing system pressures.
11	Fill zinc feeder with zinc.
12	Heat zinc vaporizer (induction) to 950 to 1000 C. Heat zinc vapor line (resistance) to 1000-1100 C.
13	Increase reactor purge flows listed for bed support, check system pressures: Zinc vaporizer/feeder - to 5 l/min SiCl <sub>4</sub> vaporizer - to 5 l/min Silicon product discharge - to maximum flow (~4-5 psi back pressure)
14	Charge weighed bed of silicon seed material (~17 lb). Increase reactor sight port purge to maximum, remove sight glass and insert silicon seed hopper. Pressurize seed hopper from sight port purge supply. Introduce bed slowly over 3-4 minute period. Remove seed hopper, close flapper valve, replace sight glass and return purge flow to normal.
15	After bed has attained reactor temperature, slowly reduce silicon product drain purge to 300-400 cc/min.
16	Recheck system pressures and bed ΔP.
17	Increase zinc flash vaporizer temperature to 1200 C.
18	Initiate ZnCl <sub>2</sub> recirculation in condenser.
19	Begin SiCl <sub>4</sub> feed to vaporizer at 200 cc/min. Reduce argon purge as vaporization rate increases to maintain purge pressure constant until minimum purge rate of 1-1.5 l/min is attained.

TABLE 3. CONTINUED.

Operation No.	Operation
20	Start zinc feeder down drive, observing time when zinc first enters zinc vaporizer. Reduce argon purge as vaporization rate increases to maintain constant back pressure until minimum purge rate of 1-1.5 l/min is attained.
21	Readjust reactor shell purges as necessary to maintain proper pressure balance.

RUN  
PROCEDURE

- 1 Maintain specified operating conditions for 8-hour period. Monitor and record temperatures, pressures, reactant and purge flows, bed  $\Delta P$ , etc. at regular intervals as indicated on record sheets. (e.g.,)
  - Reactor temperature - 927 C - bed zone
  - Zinc feed rate - 0.52 lb/min - based on feeder drive speed
  - $\text{SiCl}_4$  feed rate - 206 cc/min - liquid
  - Reactor/condenser cross-over temperature - 925 C
  - Condenser temperature - 350 C
  - Fluidized bed  $\Delta P$  - 27"  $\text{H}_2\text{O}$  (50 mm Hg)
- 2 Silicon production should be e.g., 1.89 kg/h and will cause bed  $\Delta P$  to increase. At prescribed intervals, remove silicon product from bed by intermittent opening and closing of product removal valve. Average removal rate should be 63g/min to maintain bed  $\Delta P$  at 27"  $\text{H}_2\text{O}$ . Maintain withdrawal tube purge rate at >1 l/min argon.
- 3 Samples of reaction by-products may be taken at various intervals during the run by attaching an evacuated cylinder at the ports provided. Ports are provided for sampling of:
  - Liquid effluent from condenser
  - Vapor effluent from stripper
  - Effluent from chlorination of reactor
  - Electrolytic cell exhaust gas

In order to sample the reactor freeboard for gas-phase nucleated silicon,  $\text{SiCl}_4$ , zinc and  $\text{ZnCl}_4$  concentrations, it will be necessary to remove the sight port glass and insert a sample probe through the flapper valve.

TABLE 3. CONTINUED.

Operation No.	Operation
4	At zinc feeder drive reversal, plunger reaches bottom of stroke after every 54 minutes of operation, plunger withdraws rapidly to top of stroke, while feeder refills with liquid zinc from reservoir. During this approximately 2-minute interval, no zinc is being fed to reactor. Monitor zinc feed system pressure closely, adjusting argon flow rate as necessary to prevent loss of bed support.
<u>SHUT-DOWN PROCEDURE</u>	
At conclusion of 8-hour run period:	
1	Deactivate liquid zinc feed valve (defaults to closed) during final zinc feeder downstroke. After completion of feed stroke and plunger withdrawal, deactivate feeder drive mechanism. Gradually increase argon purge flow through zinc vaporizer to 10 l/min as vaporizer inventory is depleted to maintain bed support.
2	After zinc vaporizer has emptied (indicated by decreased power consumption by Thermionic converter), turn off SiCl <sub>4</sub> feed to flash vaporizer and gradually increase argon purge flow to 10 l/min as inventory is depleted, to maintain bed support.
3	After both zinc and SiCl <sub>4</sub> are cleared from reactor, open silicon product drain valve, dropping bed into hopper. Note: Tendency for bridging of fresh seed (angular particles) requires special purge procedure, not necessary with freer flowing rounded particles of lower seed content.
4	After bed has drained, as indicated by steady bed ΔP of 1-2 in H <sub>2</sub> O, reduce argon purges through zinc and SiCl <sub>4</sub> feed systems to 0.5 to 1 l/min stand-by rate. Increase argon flow through product hopper to maximum flowmeter setting to promote cooling of drained bed.
5	Heat ZnCl <sub>2</sub> stripper to 350 C for 30 minutes to melt and drain ZnCl <sub>2</sub> accumulated during reactor operation. Turn off ZnCl <sub>2</sub> sump pump and allow condenser inventory to drain.
6	After product hopper has cooled to <100 C and with flapper valve closed, remove product hopper for emptying and seal bottom of flapper valve housing to exclude air from reactor.

TABLE 3. CONTINUED.

Operation No.	Operation
<u>ZnCl<sub>2</sub></u> <u>ELECTROLYSIS</u>	
1	Open ZnCl <sub>2</sub> storage tank drain valve; connect level probe leads in electrolytic cell; and energize automatic level control system, opening ZnCl <sub>2</sub> flow control valve.
2	Open electrolytic cell chlorine exhaust valve; energize rectifier power supply; and gradually increase cell current to 5000 to 6000 amp to begin electrolysis.
3	Energize liquid zinc overflow port heater and adjust voltage to maintain overflow port at 450-500 C.
4	Continue electrolysis for 24 hours or until ZnCl <sub>2</sub> supply from storage tank is depleted. Record cell current, voltage temperature at frequent intervals to permit cell efficiency evaluation.
5	Maintain cell temperature at 500 C by regulation of cooling water flow to anode post.
6	Collect zinc produced at overflow port in crucibles, allow to solidify and record weight of zinc collected, approximate production rate.
7	After electrolysis period has concluded (ZnCl <sub>2</sub> storage tank emptied), deactivate rectifier power supply in reverse sequence from start-up allowing auxiliary heaters to maintain cell temperature at 450 C. Reduce cooling water flow to anode post to minimize power consumption.
8	Liquid zinc overflow line from cell must either be maintained at 450 C or removed from cell and emptied to prevent breakage of quartz vessel.

Because of various limitations of equipment and procedure, to be described, the operation procedure was not carried out as outlined for a fully mature run of 8-hour duration. However, considerable progress was made in improving the operability of the equipment and identifying needs for longer range design modifications.

#### PDU Operating Experience

A total of 25 attempts at sustained operation of the PDU (except for the electrolytic cell) were made during the course of the program as summarized in Table 4. As indicated, the frequency of achieving operational status (defined as feeding both  $\text{SiCl}_4$  and Zn vapors to the fluidized bed reactor) prior to October, 1980, was very low, with only two successes out of 16 initiations. Termination of these initiations resulted from a variety of design and construction deficiencies and operational problems, the immediate causes of run termination being summarized in the table. In addition to the problems listed, numerous minor concomitant difficulties and equipment failures were experienced which have been dealt with in more detail in the preceding quarterly reports. Because many of those difficulties appeared to recur throughout the period, it was decided in late September, 1980, to cease operational attempts, evaluate the sources of these recurrent problems, and implement, as far as possible within a four- to six-week time frame, permanent or long term solutions. The difficulties identified and addressed at this time and previously during the course of the program are summarized in Table 5, along with the remedies applied. Also listed in this table for the sake of completeness and identified with an asterisk (\*) are the difficulties encountered and corrections made once operation of the PDU had been resumed.

The modifications to the PDU carried out during October and early November, 1980, served to greatly improve the reliability of the system, especially during start-up. By referring to Table 4, one can see that the frequency of achieving operational status (as defined above) was increased from 12.5% to 67% or six of nine initiations, compared to the earlier two of sixteen. The ultimate goal of sustained 8-hour operation

TABLE 4. PDU OPERATION HISTORY.

Run No.	Date	Forward Progress	Reason for Termination
1a	3/5/80	Heating reactor-condenser to operating temperature	Broken graphite flange at reactor $\text{SiCl}_4$ inlet
1b	3/6/80	Reactor at temperature, bed in place	Leak in braze joint in Therminol cooling coil on condenser
1c	3/7/80	Bed in place, starting to feed $\text{SiCl}_4$ and zinc	Zinc leak at reactor inlet, vapors escaping into furnace
2	3/27/80	Bed charged to reactor, zinc charged to feeder	Broken emergency drain on zinc liquid feeder
3	4/10/80	Feeding both zinc and $\text{SiCl}_4$ , 32-minute operation	Plugging of exhaust piping; condensed zinc in vaporizer argon purge; crack of vaporizer liquid inlet
4a	5/6/80	Reactor-condenser hot, ready to run	Unable to feed liquid zinc to feeder; drain from zinc melter plugged; heater burned out
4b	6/13/80	Reactor-condenser hot, ready to run	Purge gases by-passing condenser; insufficient heat at top of condenser
4c	6/19/80	Reactor-condenser hot, ready to charge bed	Leak in zinc vaporizer from plasma arcing; vaporizer flooded, zinc transported through reactor
5	7/17/80	System operating, feeding $\text{SiCl}_4$ and zinc for 47 minutes	Mechanical failure (binding) of zinc feeder drive broke quartz transfer tubes on feeder
6a	7/24/80	System hot, ready to charge bed	High system pressure due to marginally low temperature at top of condenser
6b	7/25/80	System hot, ready to charge bed	High system pressure due to plugging of condenser tubes with zinc dust/ $\text{ZnCl}_2$ mix; leakage of liquid zinc control valve
7a	8/21/80	System hot, feeding TET to reactor, heating zinc vaporizer to begin zinc feed	Broken quartz line between zinc feeder and vaporizer, broken argon purge inlet to vaporizer
7b	8/22/80	Reactor hot, preheating zinc vaporizer	High system pressure, insufficient temperature in condenser
8	9/5/80	System hot, bed charged and heated	High system pressure (blockage of lower part of condenser indicated); reactor flow continuity checks indicate breakage of graphite liner near TET inlet
9a	9/24/80	System heating	Leak in zinc melter; leak in Therminol heat exchanger
9b	9/26/80	System hot, heating zinc vaporizer	Excessive pressure in zinc feed system; blockage at distributor plate
10a	11/13/80	System heated, reactor-condenser junction tightened	Excessive pressure in reactor caused by zinc dust plugging it condenser vapor inlet
10b	11/20/80	34-minute operation feeding both reactants	Leak in argon purge to $\text{SiCl}_4$ vaporizer allowed reactants to block orifices in distributor plate resulting in excessive system pressure
11	11/24/80	3-minute operation feeding both reactants	Arcing from induction coil to zinc vaporizer, high argon purge pressures; zinc plenum in distributor plate found clogged with silicon sponge

TABLE 4. Continued.

Run No.	Date	Foreward Progress	Reason for Termination
12	12/10/80	5-minute operation feeding both reactants	Break within reactor furnace of quartz tube feeding Zn vapor to reactor
13	12/13/80	12-minute operation feeding both reactants	Excessive system pressure, smoking from reactor furnace caused by plugging of exhaust tubing downstream from condenser; evidence of $\text{SiCl}_4$ leakage between reactor shell and graphite liner
14	1/8/81	System heated to operating temperature; purge flows increased for pressure check; Zn feeder charged	Malfunction in Zn automatic flow control overfilled feeder and vaporizer and allowed Zn to enter reactor and condense in product drain, condenser inlet
15	1/20/81	System heated; bed charged and heating	Rapid pressure rise caused by plug at condenser exhaust ruptured Zn vapor tube at reactor inlet connection
16	1/23/81	41-minute operation feeding both reactants; Zn feeder recycle	Zn vaporizer failed to refill on plunger recycle - Zn valve failed to open; crack discovered in Zn vaporizer
17	2/2/81	9-minute operation feeding both reactants	Leak in Zn vapor tube evidenced by smoking within reactor furnace; high pressure in $\text{SiCl}_4$ feed system

TABLE 3 MODIFICATIONS OF PDU EQUIPMENT AND OPERATION.

Problem	Corrector
1. FLUID ZEP-BED REACTOR	
1. Leakage of zinc vapor at the reactor inlet adaptor	Redesign inlet adaptor to isolate the primary quartz-graphite seal from thermal expansion movement of reactor shell, added two secondary seals to exclude air from the system
2. Breakage of graphite reactor nozzles	<p>(a) Replaced stiff expansion bellows with more flexible ones</p> <p>(b) Installed support arms for positive control of motion at the reactor/condenser connection</p> <p>(c) Increased diameter of inlet shell surrounding SiCl<sub>4</sub> inlet nozzle to accommodate expected relative movement between shell and graphite liner during thermal transients.</p> <p>(d) Improved design of joint between graphite SiCl<sub>4</sub> inlet nozzle liner and reactor liner to improve mechanical strength, provide more positive seal</p>
3. Degradation of stainless steel reactor shell by ZnCl <sub>2</sub>	<p>(a) Replaced major portions of shell and bellows</p> <p>(b) Improved seals between graphite liner components</p> <p>(c) Increased reactor shell purge flow to inhibit out-leak of ZnCl<sub>2</sub> vapors</p>
4. Degradation of reactor graphite liner	<p>(a) Increased argon purge capacity to reactor shell</p> <p>(b) Improved seals between graphite liner components</p>
5. Difficulty draining silicon bed/product from reactor	<p>(a) Modified construction of product drain tube sections to eliminate potential shivers or re-entrant angles at joints between tube sections</p> <p>(b) Modified procedure for charging bed to reactor to prevent filling of discharge tube before bed achieved reaction temperature</p>
6. Leakage of by-product gases at flanged reactor exhaust/condenser inlet connection due to minor misalignment between vessels	Two-part graphite intermediate flange ring having a spherical interface between its mating halves was constructed to accommodate both radial and axial misalignment between reactor and condenser
7. Binding of the upper (expanded) section of the graphite reactor with the stainless steel shell	<p>(a) Reactor was heated under lateral stress for a 72-hour period to remove thermal-expansion-induced warpage in the expanded shell section</p> <p>(b) Reactor support pads were modified to more adequately accommodate radial thermal expansion of reactor shell</p>
8. Breakage of the quartz zinc-vapor inlet tube during reactor cool-down	<p>(a) Redesigned quartz tube to include a helical coil around the reactor body to better accommodate the 0.150-inch vertical movement of the zinc inlet adaptor during reactor heating and cooling</p> <p>(b) Increased radius of curvature and thickness of quartz tube at zinc inlet adaptor for increased strength</p> <p>(c) Increased rigidity of zinc vaporizer support cradle.</p>

TABLE 5. Continued.

Problem	Correction
*9. Continued excessive pressure within the $\text{SiCl}_4$ vapor feed system.	Enlarged $\text{SiCl}_4$ inlet ports in reactor distributor plate to 0.147 inches to correct an original machining error made during reactor fabrication
II. BY-PRODUCT CONDENSER	
1. Desired temperature within condenser difficult to achieve and maintain during PDU start-up	(a) Thermocouple and auxiliary electrical heating were added to top end of condenser
2. Inability to maintain pressure balance between condenser and argon-purged sump tank	(b) Increased thermal insulation of condenser
3. Insufficient flow of molten $\text{ZnCl}_2/\text{Zn}/\text{Si}$ by-product mixture from condenser reservoir to sump tank	Pressure equalization tube installed between sump tank and condenser above equilibrium liquid level
4. Loss of liquid seal at condenser pass-separator on start-up of the recirculating sump pump	Liquid drain tube from condenser to sump tank was enlarged from 3/4-in I.D. to 1-1/2-in I.D. to compensate for higher-than-expected viscosity of the molten salt mixture
5. Inability to monitor level of $\text{ZnCl}_2$ or adequacy of its recirculation within the condenser	Volume of $\text{ZnCl}_2$ sump tank was approximately doubled to reduce liquid level drop at pump start-up based on modification of original design estimate of system hold-up
6. Intermittent blockage of condenser outlet creating high system pressures	Level probes were added to the condenser sump tank at appropriate heights to permit inference of pumping rate and condenser inventory. Replaced broken graphite liner of condenser outlet nozzle and added locking wire to prevent inward movement of liner against pass separator plate in event of future nozzle breakage
III. ZINC FEED SYSTEM	
1. Leakage of liquid zinc from joints in the graphite piping	Zinc flow control valve was repositioned directly under the melt tank eliminating two feet of graphite piping and two cemented graphite joints from the system
2. Breakage of quartz tubes connecting the vaporizer, zinc feeder, and valve	(a) Displacement feeder support structure was substantially strengthened and braced to eliminate mobility of the feeder vessel relative to the valve and vaporizer and to prevent off-axis movement of the feeder drive mechanism (b) Zinc vaporizer support structure was changed to increase rigidity of support and improve adjustability during system assembly
*3. Chatter in zinc flow control valve (continued rapid opening and closing), failure of valve to close automatically after filling feeder	Relocated electrical circuit controlling valve operation through molten zinc to eliminate zinc valve from the circuit; a gas bubble trapped in quartz tubing between valve and feeder caused intermittent continuity

TABLE 5. Continued.

Problem	Correction
IV. AUXILIARY EQUIPMENT	
1. Flooding in the $\text{SiCl}_4$ vaporizer	Baffle plate was added to the $\text{SiCl}_4$ liquid inlet to redirect flow against the heated walls of the packed bed vaporizer
2. Plugging of vapor exhaust piping	<p>(a) Heat tracing was added to prevent fogging and deposition of <math>\text{ZnCl}_2</math> vapors carried through the stripper</p> <p>(b) Large trap was added to allow excess <math>\text{SiCl}_4</math> vapors to condense and "drop out" for draining before reaching the neutralizer drums</p>

of the system was not achieved within the contract period, however, since a new generation of operational problems was disclosed and inherent system weaknesses which could not be remedied within the scope of the project effort remained.

Although most of the problems immediately responsible for the termination of operating trials were addressed and corrected as they occurred, the underlying problem of general deterioration of the reactor could not be overcome. As the result of this situation and in spite of considerable improvement being made in the operability of the PDU, adequate evaluation of the four major components was not accomplished as planned. Comments on the status of these units at the end of the PDU program are included in the following section of this report.

#### Status of Operability of the Four Critical PDU Units

##### Zinc Vaporizer and Feed System

Initial operation in the PDU of the direct-induction-coupled zinc vaporizer pictured in Figure 11 revealed limitations that were not encountered in an earlier laboratory-scale design-rate test of the concept<sup>(2)</sup>. These limitations were related to the less efficient coupling obtained with the larger induction coil (used to provide for thicker insulation) and the formation of a parasitic plasma in the vapor phase which did not permit sufficient coupling to the zinc to achieve the design rate of vaporization.

Although solutions to these problems eventually emerged as the result of experimental work described in this report, it was decided prior to that time to defer attempts to use the direct-coupled vaporizer in the PDU and return to a scaled-up version of the graphite-tray "flash vaporizer" used previously in the Miniplant. As pictured in Figures 14, 15, and 16, the vaporizer was fed with liquid zinc from a reservoir by displacement with a descending piston.

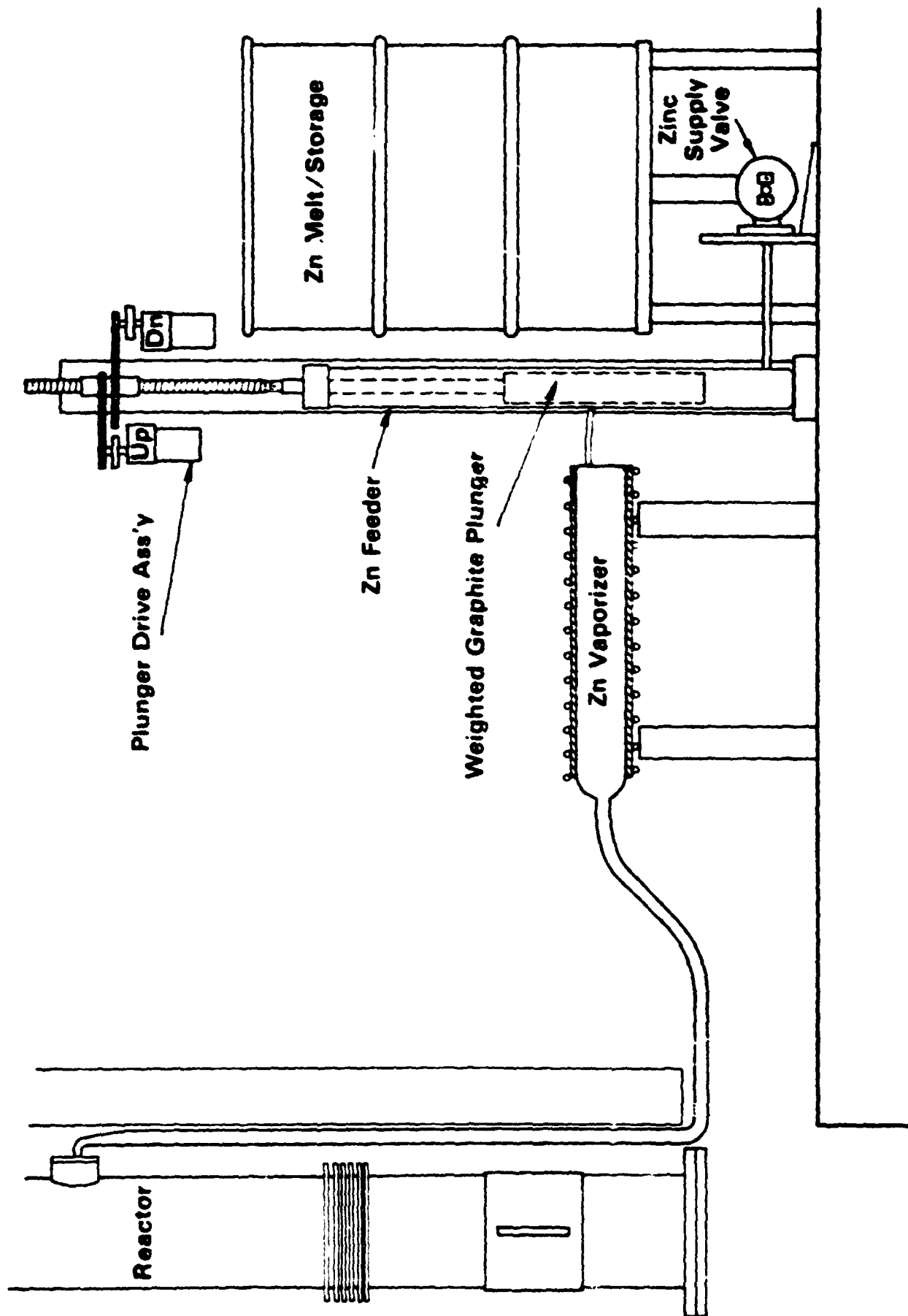


FIGURE 14. ALTERNATIVE ZINC FEED SYSTEM

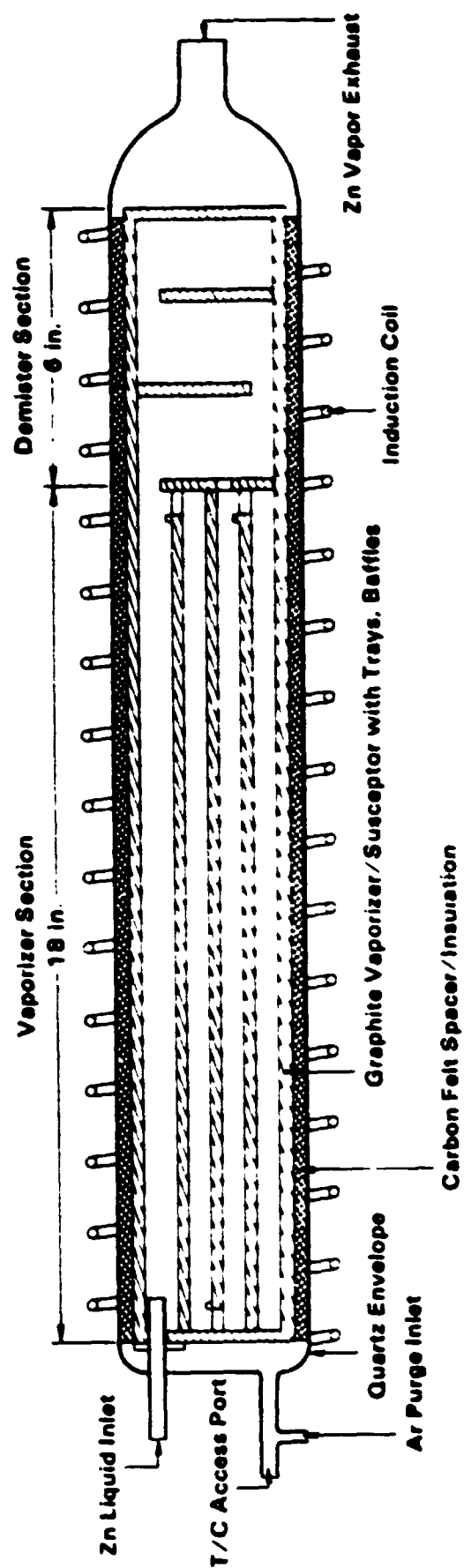


FIGURE 15. GRAPHITE TRAY ZINC VAPORIZER

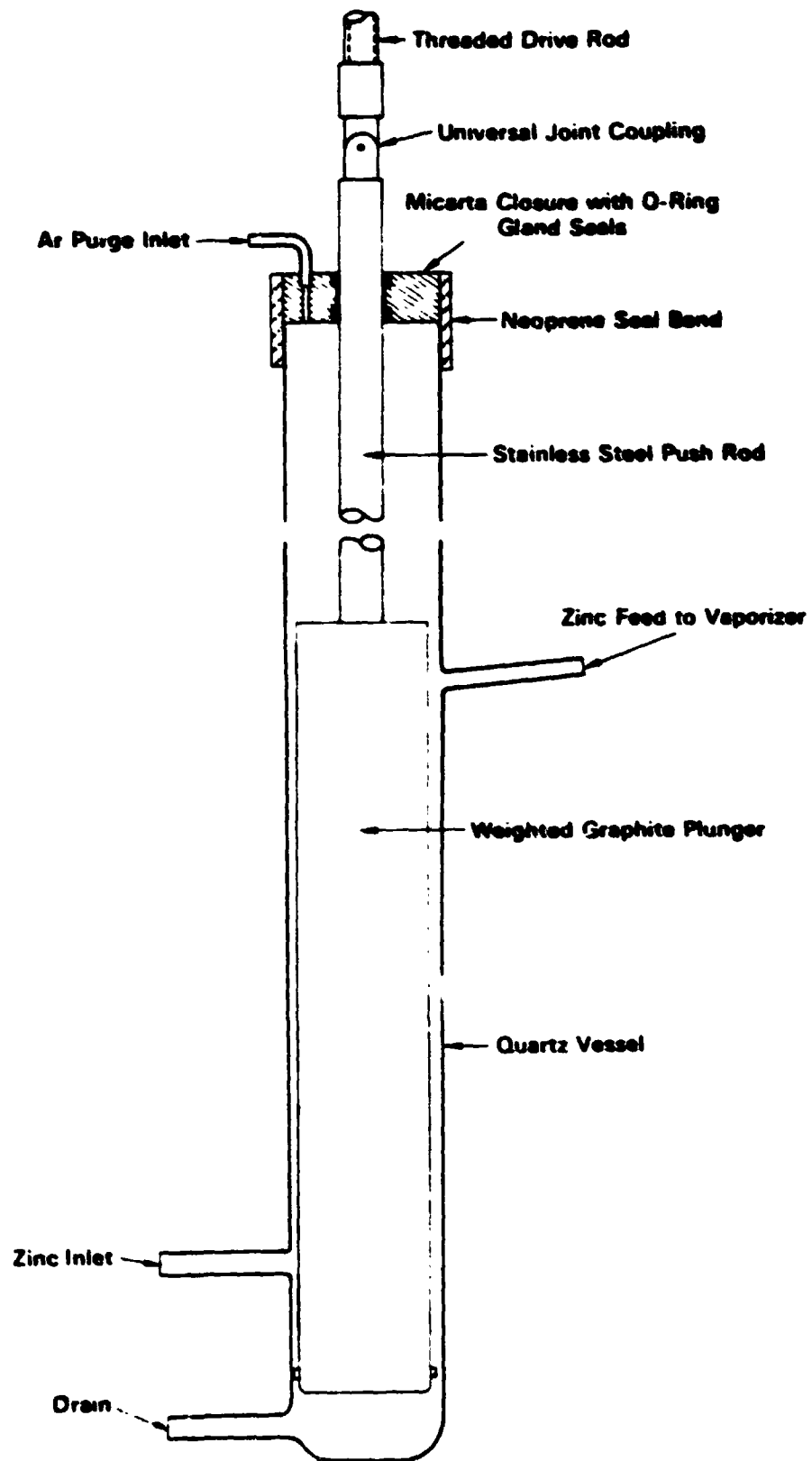


FIGURE 16. LIQUID ZINC DISPLACEMENT FEEDER

Although this alternative vaporizer had the disadvantage of greater lag in response of vapor flow to a change in liquid feed rate, it was believed that the PDU could be operated reliably with it, pending development of the more desirable direct-coupled vaporizer. However, despite the fact that the displacement-fed graphite-tray vaporizer was operated on several occasions at feed rates of up to 50 percent of design, the operation was not without its own set of problems, most of which appeared to be mechanical. These include:

1. Breakage of quartz tubing between valve and feeder, feeder and vaporizer, and from vaporizer to reactor
2. Leakage of zinc at the graphite control valve:
  - a. past the valve seat
  - b. through graphite/graphite and graphite/quartz joints
  - c. through Grafoil-packed joints
3. Deterioration by oxidation of graphite lines and parts from exposure to air at 500 C, despite isolation with an argon blanket.

A further reservation with regard to the long-term operability of the zinc-feed system is the fact that the recharging of the displacement reservoir was never carried out routinely during a run. In most cases this resulted from shutdown being dictated by other factors unrelated to the operation of the zinc feed system, and does not preclude routine recharging.

Although improvements were made in the operation of the zinc feed system during the course of the program with respect to the deficiencies listed above, it is believed that further refinements will be in order before operation of the system can be classified as routine.

#### Fluidized-Bed Reactor

Operation of the PDU showed that appropriate fluidization of the particle bed could be maintained at zinc vapor and  $\text{SiCl}_4$  feed rates of at least one-half of design rate, the maximum explored. However, such

operation was not maintained for sufficient periods of time to obtain reliable data on the efficiency of conversion of  $\text{SiCl}_4$  which could be compared with theoretical predictions and with Miniplant experience.

A significant accomplishment with the fluidized bed reactor was the frequent demonstration of withdrawal of the fluidized bed from the bottom of the reactor. However, such withdrawal has yet to be made during flow of the reactants, and the importance of keeping zinc out of the product withdrawal tube on such occasions was demonstrated when zinc inadvertently entered the product withdrawal tube resulting in solidification and immobility of the mass of silicon within the withdrawal tube.

By far the most serious limitation of the fluidized bed reactor as presently designed relates to the provisions made for isolating the hot (925 C) graphite reactor from ambient to prevent air oxidation. Enclosure by a stainless steel shell was chosen as a reasonable expedient. However, this choice was accompanied by two problems:

1. Although provisions were made for the control and accommodation of differential thermal expansion between the graphite reactor and the stainless steel shell, such provisions were not adequate to avoid frequent breakage of the upper and lower graphite appendages of the reactor. Part of the problem is suspected to have been related to creep of the stainless steel shell, as some progressive permanent distortions were observed. Further, it is suspected that residual torsional stresses left after unannealed welding of the shell led to unpredictable lateral displacements during heating and cooling.
2. The thin stainless steel bellows used to accommodate thermal expansion differentials were subject to corrosion by zinc and/or zinc chloride which inadvertently entered the annulus between the shell and the reactor. Unless such intrusion can be prevented, it appears that

a stainless steel jacket is impractical for this application.

The problem of thermal expansion-induced breakage would be minimized once normal operation is achieved and the frequent heating/cooling cycles experienced with the PDU can be avoided. Improvements in provisions for isolating zinc and zinc chloride from the annulus can undoubtedly be made. Accordingly, the design of the reactor should be reviewed with the objective of identifying designs which would better insure this isolation or provide improved corrosion resistance. One such design would be based on quartz, a material inert to both the reaction species and to air.

#### By-Product Condenser

The wetted-wall condenser of the PDU is designed to condense the by-product zinc chloride as a liquid and the unreacted zinc as a suspended solid for return to the electrolytic cell. The zinc chloride stripper is provided to handle the zinc chloride that escapes the wetted-wall condenser [0.7g/hr under the conditions of Figure 8 if the zinc chloride content of the exit gas ( $\text{SiCl}_4 + \text{Ar}$ ) from the condenser is brought to equilibrium with the condenser wall at 350 C].

Owing to the short cycles of operation of the PDU, it was not possible to obtain quantitative data on the efficiency of operation of this condenser system. Although progress was made in eliminating some recognizable causes of inefficient condensation (by-passing of the condenser pass plate due to low  $\text{ZnCl}_2$  level, etc.), problems with unexplained downstream plugging during operation at only 50 percent of design capacity remained at the end of the program which left open the question of the basic design of the  $\text{Zn}/\text{ZnCl}_2$  condenser as it relates to condensation efficiency.

The condenser must quench the reaction by-product mixture so that continued reaction of  $\text{SiCl}_4$  with liquid zinc to form a mass of silicon needles is prevented. However, quenching must not be so great as to create  $\text{ZnCl}_2$  fog which is entrained in the off gas and is thus not subject to controlled removal.

An alternative to the present design that would avoid fogging is a condenser operating closer to equilibrium, i.e., at a higher surface temperature and with correspondingly greater heat transfer area. It will be recalled that such a concept was initially incorporated in the EPSDU design but was later abandoned in favor of the lower temperature condenser which had the advantages that (1) the zinc chloride, provided to wet the condenser wall, could be recycled in direct contact with stainless steel, thus avoiding graphite lining of the equipment, and (2) the by-product mixture would be most effectively quenched, thus avoiding the formation of silicon needles.

As these advantages are still compelling, a definitive answer as to the condensation efficiency of the present low-temperature condenser should be obtained so as to confirm its feasibility, before use of the less desirable high-temperature design is again considered.

From the limited experience with the recirculation of the  $\text{ZnCl}_2$  in the wetted-wall condenser after modification, it can be concluded that:

- (1) Liquid  $\text{ZnCl}_2$  can be recirculated through the system at close to design rate
- (2) Temperature of recirculating  $\text{ZnCl}_2$  can be maintained at 350-360 C by the Therminol and external sump tank heater
- (3) Design of the vertical cantilever pump appeared satisfactory:
  - (a) little or no leakage at purged seal
  - (b) pumping rate satisfactory
  - (c) stainless steel held up well in environment of molten  $\text{ZnCl}_2$

It is of course possible that neither the low-temperature nor the high-temperature condenser may be satisfactory because of  $\text{ZnCl}_2$  fog generation in the first case and silicon needle generation in the second case. If that should be true, the alternative of quenching the by-product with liquid  $\text{SiCl}_4$  to form a slurry for later separation should be considered.

#### Electrolytic Cell

Just as the limited accumulated PDU run time precluded full testing of the wetted-wall condenser, evaluation of the electrolytic cell was limited. Although operation of the cell with solids-free  $\text{ZnCl}_2 + \text{KCl}$  was at one time contemplated, it was believed best to await the accumulation of a full charge of reaction product  $\text{ZnCl}_2 (+ \text{Zn}, + \text{Si})$  so that the effect of suspended zinc and silicon on the cell operation could be studied. As the full charge was never available, the evaluation did not reach that point.

Despite the limited evaluation of the electrolytic cell, it is believed that, on the basis of recent Bureau of Mines experience with protracted operation of a 2000-amp cell<sup>(8a)</sup>, its operation should be one of the less troublesome aspects of the system once operability of the PDU is established.

## PROCESS DISCUSSION

Experience with the PDU operation on the present program has been discussed above as it relates to the status of operability of the four critical units of the PDU. It remains to summarize this experience and relate it to other aspects of the overall process so that recommendations can be made for further development.

During the course of the PDU program a large number of design, equipment and procedural problems were solved which brought the program closer to the goal of routine 28-hour batch operation for the accumulation of engineering data on the four basic units being evaluated. However, owing to residual problems, that goal was not reached and several aspects of the process need to be given additional attention.

The following summarizes the status of the various sections of the process and the requirements for further development:

### SiCl<sub>4</sub> Production

The technology for SiCl<sub>4</sub> production from chlorine and silicon carbide has been developed adequately for commercial operation by several manufacturers.

- The design of equipment and operating procedures would be obtained from those in the industry familiar with it.

### SiCl<sub>4</sub> Purification

The design of the SiCl<sub>4</sub> purification section of the 50 MT/year EPSDU has been based on standard practice.

- Use of the EPSDU design of the SiCl<sub>4</sub> purification section should involve no more than the usual minor problems associated with start-up of a petrochemical operation.

### Zinc Vaporization

The zinc vaporizer used in the PDU was shown to be workable. The feasibility of the direct-coupled induction-heated vaporizer was demonstrated in the laboratory. This concept obviates the need for the

rechargeable reservoir and presents other advantage .

- Future process development should include substitution of the direct-coupled vaporizer and provisions for increasing the ruggedness of the quartz zinc-transfer lines.

#### SiCl<sub>4</sub> Vaporizer

After improving the distribution of the entering liquid SiCl<sub>4</sub>, no problems remained with the SiCl<sub>4</sub> vaporizer of the PDU.

- The present SiCl<sub>4</sub> vaporizer should be adequate for future use in the PDU. A direct-heated boiler would be used in a larger installation (EPSDU).

#### SiCl<sub>4</sub> Preheater

As far as could be determined by the PDU operation, the SiCl<sub>4</sub> preheater performed according to design. However, the implications of inadequate preheating are sufficiently subtle that more experience would be required to confirm adequacy.

- The present preheater design appears to be adequate for future use.

#### Fluidized-Bed Reactor

PDU operation disclosed limitations of the present reactor design with regard to provisions for thermal expansion differentials and protection of the graphite liner from the ambient.

- Further work with the process at the PDU scale should be carried out with a quartz reactor if it is not possible to conceive design changes that would correct the limitations of the present reactor.

#### Product Withdrawal System

The product withdrawal system was used to discharge the fluidized bed on several occasions, but not during production. Prevention of zinc vapor intrusion is imperative.

- Prevention of zinc vapor intrusion by designed use of purge gas must be evaluated in future work; alternatively,

provision could be made for periodically interrupting zinc flow (substituting argon for fluidization) during product removal.

#### Zn/ZnCl<sub>2</sub> By-Product Condenser

Adequacy of the by-product condenser for quenching the reduction reaction (avoiding Si needle formation) without fogging out ZnCl<sub>2</sub> (and Zn) has not been tested in limited PDU operation.

- Continued PDU work would include evaluation of present and possibly alternative condenser designs.

#### Zn/ZnCl<sub>2</sub> Storage

Although the anticipated large amounts of condensate were not handled in the PDU operation, the present tank for intermediate storage is tentatively judged to be adequate. Settling and immobilization of suspended zinc over a long period of time remains a concern.

- Validation of the mobility of Zn/ZnCl<sub>2</sub> in and out of the storage tank, and its protracted corrosion-free storage, must be undertaken in future work.

#### ZnCl<sub>2</sub> Electrolysis

Limited operation of the PDU did not generate sufficient quantities of ZnCl<sub>2</sub> (containing suspended zinc and silicon) to permit evaluation of the electrolysis cell on the present program. However, success with large ZnCl<sub>2</sub> electrolysis cells at the Bureau of Mines encourages the continued use of this concept.

- Future development would include the verification of the design of the ZnCl<sub>2</sub> electrolysis cell with particular attention to the adequacy of chlorination of the suspended silicon.

#### Waste Disposal

The present system for disposing of waste SiCl<sub>4</sub> and chlorine is judged to be adequate, although subject to improvement.

- Use of the present waste disposal system would be continued in future development work in the PDU but a more automated system would be used in a larger installation (EPSDU).

#### Chlorination of Wall Deposit

Although the chlorination of deposited silicon and errant zinc was carried out for the removal of constrictions on several occasions in the PDU program, the growth of significant wall deposits and their controlled chlorination were not involved in the limited PDU operation.

- Controlled chlorination of wall deposits would be subject to investigation in future development work.

In summary, although progress has been made, problems remain and the future of the fluidized-bed zinc vapor reduction of  $\text{SiCl}_4$  will depend upon the evolution of a suitable alternative design for the fluidized-bed reactor and a verification of adequate performance of the units whose designs have not yet been fully tested.

#### RECOMMENDATIONS

It is recommended that the next step in development of the process be the design of an alternative fluidized-bed reactor, based on quartz construction or an alternative, and the incorporation of that reactor in the PDU equipment, to be operated with the objectives adopted for the present program. The results of that operation should then support a basic decision on the overall feasibility of the process and of the equipment for carrying out its operation commercially.

## EXPERIMENTAL SUPPORT

During the course of the Phase-III program, whose major emphasis was on the PDU activities, a complementary experimental support program was maintained which dealt with problems related to the PDU, but which could be solved independently of its operation. The following items were given attention to a greater or lesser degree:

- (1) Determination of product quality.
- (2) Outgassing of residual zinc from product granules.
- (3) Volatilization of impurities from the zinc vaporizer.
- (4) Heating the zinc vaporizer by direct-coupled RF.
- (5) Mock-up of wetted-wall condenser.
- (6) Segregation of large particles in fluidized bed.
- (7) Performance of electrolytic cell.

These subjects will be discussed in turn.

### Product Quality

Data on product quality were presented in the Phase I/II Final Report<sup>(1)</sup> which indicated that with the exception of residual zinc, to be discussed later, the measurable impurities of the zinc-reduction product were in the low ppmw level. No additional definitive data on product quality were obtained at BCL during the Phase-III period covered by this report. However, it is significant to record that solar cells fabricated by Westinghouse<sup>(9)</sup> from a web dendrite made from the product of Run 97 of the BCL Miniplant exhibited 12.8 AM-1 efficiency\*.

Although the Run-97 product was given a 6-hour heat treatment in argon by Westinghouse in an effort to remove the 1470 ppm residual zinc, the material was in other respects handled in the same way as the practice for their semiconductor-grade feed, and gave comparable results. The major difference was that the resistivity of the intentionally doped material (0.24  $\mu$ -cm vs.

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\* Corrected for the expected effect of providing an antireflective coating.

9  $\Omega$ -cm calculated) indicated some degree of autodoping, the source of which would be of interest to identify in future work with the product. The granular form of the product (See Figure 17) is generally viewed as being convenient for subsequent handling.

#### Elimination of Residual Zinc

The presence of residual zinc in the Miniplant product and its implications were discussed in prior Quarterly Progress Reports (10, 11) and a detailed analysis of its removal by heat treatment was given(12). Accordingly, this report is limited to the presentation of one additional item of related data and a summary of the conclusions.

The level of residual zinc in the Miniplant product ranged from a few hundred to a few thousand ppmw, depending upon the conditions of preparation. The probability that much of the residual zinc in the "high-zinc" samples originated as occluded zinc mist droplets from the flash vaporizer used in the Miniplant is supported by the presence of large quantities of residual zinc in silicon-encapsulated agglomerates of several particles. In one run for example, such agglomerates of from perhaps 20 to 50 granules constituted 0.2 percent of the product.

Although the zinc-mist theory is attractive, the effect of capillarity in a microporous structure should not be overlooked. Based on published equations(13) for the lowering of the vapor pressure of a liquid absorbed in capillaries, the tendency for spontaneous evaporation of any occluded zinc can be negated in a 1-atm ambient at several degrees above the normal boiling point in a structure with pores  $>0.1\mu\text{m}$ .

Conversely, zinc can be condensed into pores at temperatures several degrees above the normal boiling point (e.g., 10 degrees C for  $0.03\mu\text{m}$  pores) from an ambient containing zinc at a partial pressure of one atmosphere. If it were not for the clear evidence of the participation of zinc droplets in the formation of the agglomerates noted above, one might be tempted to assign the zinc occlusion mechanism entirely to non-equilibrium condensation in pores.



FIGURE 17. MINIPLANT PRODUCT GRANULES

### Prospects for Decreasing the Residual Zinc Content of the Product

If the above-suggested droplet entrainment mechanism for the occlusion of zinc in the product is valid, two levels of improvement can be anticipated. In the first place, providing for the disentrainment of the large zinc mist droplets can be expected to decrease the residual zinc content dramatically by assuring instant evaporation of the surviving smaller zinc droplets on contact with the silicon particles. Secondly, decreasing the quantity of zinc that is carried to the fluidized bed as a mist will not only decrease the quantity of occluded residual zinc, but will decrease proportionately the residue of other non-volatile contaminants carried in the zinc mist.

It should be noted that the zinc vaporization and transfer system in the PDU provided a greater opportunity (much longer line) for the evaporation of mist droplets than was provided in the Miniplant. Further, some packing was provided for disentrainment by impingement. However, the line velocities were somewhat higher than in the Miniplant, so it is not possible to predict the net effect on mist generation and transport. Unfortunately, no data were obtained on the zinc content of material deposited in the PDU because the run conditions were not well enough established in the short runs to make such data reliable.

Despite the absence of data and the necessity of conjecture, it is believed that the zinc content of a properly designed and operating facility would be in the 100 ppmw range. To go below that point one has the options of removing the residual zinc by:

- (1) Heat treatment of the product in vacuum or inert gas below the melting point, or
- (2) Melting the product (data presented in the Phase I/II Final Report<sup>(1)</sup> indicated that the zinc level could be driven to <10 ppm by this treatment).

Either of these options carried out as part of the silicon-production process would add cost. Further, the second option obviates the advantage of the free-flowing granular form of the present product and is therefore rejected as a solution to the problem. Thus the first option,

being the least undesirable, was considered and experiments were carried out, as discussed later, to obtain data that would permit extrapolation from the Miniplant-size particles (400 $\mu$ m) to the larger size (e.g., 800 $\mu$ m) expected in a commercial operation. However, it is believed prudent to consider seriously the implications of not removing residual zinc from the product granules.

#### Implications of Not Removing the Zinc

Although leaving up to 100 ppmw of an impurity in a supposedly high-purity product is psychologically disturbing, the option is worthy of critical evaluation because no cost is added. If it can be assumed, as appears likely, that fusion of the silicon is effective in eliminating the zinc, and that the ingot-, ribbon-, or sheet-growing processes all provide the conditions necessary for zinc removal, one need only question the consequences of the zinc evolution. Zinc evolution will obviously add to the products of outgassing inherent in any of these operations, and the relative amount added will depend upon the quantity of zinc being handled.

In the growth of single-crystal ingots by the Czochralski process, care is taken, by means of suitably directed inert sweep gases, to prevent the condensation of SiO [from the reaction with the crucible,  $\text{Si(l)} + \text{SiO}_2\text{(s)} = 2\text{SiO(g)}$ ] at locations that would permit its falling back into the melt, and similar precautions would appear to be appropriate for any zinc evolved in the process.

However, a number of processes being considered by the LSA project either do not have that restriction, or provide for physical isolation of the melting process from the growth area, which obviates the problem with regard to zinc.

Fall-back of condensed zinc is obviously of no concern in the Heat Exchange Method (HEM) of ingot growth being studied by Crystal Systems, Inc.,<sup>(14)</sup> and conversations with members of their staff have indicated that the granular form of the BCL product would be eminently suitable for their use, despite its zinc content. The same should be true of the isolated melt replenishment processes being studied by others, provided the condensed zinc does not overly tax the provisions already available for handling the condensed materials.

Since all of the sheet processes now under consideration involve the use of quartz crucibles for melting the silicon and holding it during the growth process, all are subject to the evolution of SiO(g) and condensation of this material at some point. The key to the acceptability of zinc evolution is the quantity of evolved zinc relative to evolved SiO. Thus, an analysis of this ratio was undertaken for a typical Czochralski process, as discussed in the Twentieth Quarterly Progress Report(12).

As an example, consider 12 Kg of liquid silicon (4800 cc) in a 18-cm diameter crucible filled to the 19-cm level, from which a 12-cm diameter ingot is pulled in 4 hours. Assuming that the crucible is exposed to the molten silicon on the average of one hour during an assumed 2-hour melt time and 2 hours during the 4-hour pull time, or a total of  $t = 180$  minutes, one can calculate the ratio of zinc to SiO volume as a function of zinc content of the silicon. These results indicate that at or below the 100 ppm level (where the ratio of the zinc to SiO volume is 0.05), it may even be difficult to detect the zinc evolution. Zinc at that level would certainly appear to place no significant additional burden on cleaning the apparatus.

It should be noted that zinc condensate may even be less detrimental to the crystal growth process than SiO condensate, in that when a particle of zinc drops to the surface of the melt, it can be expected to evaporate quickly rather than possibly float to the growth interface and disrupt the growth mechanism as occurs with SiO particles. Moreover, the zinc being evolved primarily in the melting step should be covered over with SiO during the pull.

In light of the above, it is recommended that those concerned with the ingot-, sheet-, or web-forming processes give serious consideration to investigation of the use of the BCL-process silicon in the "as-is" condition once sufficient quantities are available.

#### Heat Treatment Experiments

As noted above, the most attractive option for removal of residual zinc as part of the silicon production process is outgassing at some temperature below the melting point of silicon.

It was reasoned that the transport of zinc from the body of the granule to the exterior would be rate limiting whether vacuum or an inert

sweep gas is used to remove the zinc evolved in a heat treatment. Accordingly, as described in the Eighteenth Quarterly Progress Report<sup>(11)</sup>, samples of Mini-plant product (~400 $\mu$ m dia) in evacuated quartz tubes were heat treated as a function of time and temperature.

In order for these data to be useful in predicting the outgassing behavior of the larger (800-1000 $\mu$ m) product granules expected eventually, a model was needed for the zinc transport which adequately describes the outgassing behavior of the present samples. Models available in the literature which describe the outgassing of spherical particles have two limitations for the present use:

- (1) Solubility of the diffusing species (or strong absorption) is assumed such that a monotonic concentration gradient exists along the radius of the granule which changes progressively with time, and
- (2) No provision is made for the presence of a zinc-free core.

By contrast:

- (1) The zinc is present in quantities considerably above the solubility limit (e.g., 0.03 ppmw at 900 C), and
- (2) The available samples have zinc-free cores (27 v/o for Run 50, 12 v/o for Run 96).

Further, the indication of porosity implicit in the temperature rise on exposure of outgassed particles to air (see the Sixteenth/Seventeenth Quarterly Progress Report<sup>(10)</sup> for details) suggests that the model take into consideration various possible conditions relative to the porosity of the granules.

Three cases have been considered:

Model A ~ Zinc highly dispersed as a second phase in spherical particles; rate of outgassing limited by diffusion through the silicon between the retreating two-phase front and the outer surface.

Model B - Zinc trapped in silicon surrounding pores of connected porosity; rate of outgassing limited by diffusion through the silicon surrounding the pores; negligible resistance to flow in the connected pores.

Model C - Zinc contained solely in connected porosity which is filled with zinc; rate of outgassing limited by the permeability of the connected porosity.

The derivation of equations relating outgassing time for these models is detailed in the Twentieth Quarterly Progress Report<sup>(12)</sup>.

#### Results of the Heat Treatment Data

##### Model A

The large discrepancy in the apparent diffusion coefficient for the high- and low-zinc samples, plus the lower-than-predicted rate of initial outgassing, led to the rejection of Model A as a valid representation of the zinc transport.

##### Model B

In treating the data in accordance with Model B, it was necessary to enter values for pore size and volume fraction of porosity. For the same assumed pore size and porosity, the data were in disagreement. However, agreement could be obtained by assuming different pore-size/porosity combinations for the two samples studied. This is not totally unreasonable for samples of widely different zinc content. Further, the porosities (e.g., 2 percent) and pore sizes (e.g., 1.5-3.4 $\mu$ m) that fit the data when the published value of diffusivity<sup>(15)</sup> is used, seem to be consistent with what one sees in the particle cross-sections (however, no statistical count and measurement of pores was made).

To obtain information on the porosity of the Miniplant product, a single measurement with the mercury porosimeter was made on the granules from Run 50 after 256 hours outgassing at 900 C. The results, given in Table 6,

TABLE 6. MERCURY POROSIMETER MEASUREMENT OF  
RUN-50 MATERIAL AFTER 256 HOURS IN  
VACUUM AT 900 C.

Pressure, psig	Diameter of Pores Penetrated, $\mu\text{m}^*$	Volume Change, %
14.7	15	0
29.4	7.5	0
↓	↓	↓
3527	0.062	0.7
↓	↓	↓
4115	0.053	0.7
4409	0.050	2.8
↓	↓	↓
10,287	0.021	2.8
10,875	0.020	3.5
↓	↓	↓
14,696 (end)	0.014	3.5

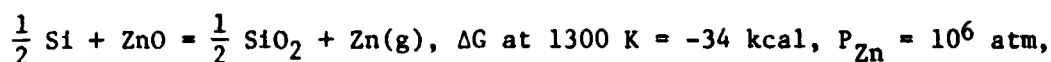
\* On the assumption of zero wetting.

suggest that the bulk of the connected porosity (indicated to be ~3 percent\*) is in the range of 0.05 $\mu$ m diameter and below, i.e., inconsistent with the requirements for the Model-B treatment. The porosimeter data are, however, more consistent with the heat effect observed when the products of Runs 97 and 98 of the Miniplant were exposed to air after vacuum outgassing<sup>(10)</sup>. The observed 70 C spontaneous temperature rise corresponds to oxidation of 0.17 percent of the silicon (adiabatic treatment). If this material is assumed to constitute the walls of the pores indicated by the data of Table 6, it corresponds to the oxidation of 4 monolayers of silicon. By contrast, if the oxidizable area is represented by the porosity indicated by the treatment by Model B, the heat generation corresponds to the oxidation of from 500 to 1800 monolayers, values difficult to reconcile with the observed rapidity of the heat evolution.

A further deficiency of the Model-B treatment is the low outgassing rate at the later stages of outgassing relative to that predicted. Part of that discrepancy might be resolved by the assumption of a mixture of widely different pore sizes, rather than an average uniform pore size.

It is also possible that the lag in outgassing is related to an entirely different phenomenon, i.e., the presence of a less mobile form of zinc in the particles. Whereas the data of one experiment at 1050 C extrapolated to complete outgassing at from ~30 to ~40 hours, depending upon the model used, about 20 ppmw zinc was found to remain at 75, 100, and 125 hours. This suggests that residual zinc at the 20 ppmw level was present in a less mobile form, possibly as the oxide resulting from superficial air oxidation on exposure of the sample to air.

Although elemental silicon would be expected to reduce zinc oxide according to



it is probable that a similar superficial oxide film on the silicon would seriously limit such a reaction kinetically.

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\* If this porosity is confirmed, the indication of negligible porosity in earlier measurements with the xylene pycnometer<sup>(1)</sup> would have to be explained by penetration of the porosity by the xylene.

It is not inconceivable that the kinetics of the above reaction contributed significantly to the rate of zinc evolution in all of the experiments. However, this complication has not been explored. Its presence may explain some of the discrepancies.

#### Model C

Model C assumed that the zinc fully occupies the connected porosity. On this basis, the porosity is proportional to the zinc content and this compensation allows for the similarity of the outgassing behavior of samples with an almost 10-fold difference in zinc content. The difficulty with this model is that it allows for a connected porosity of only ~0.03 percent for the material from one run and only ~0.3 percent for that of the other run. Any porosity in excess of that must be closed porosity for the model to be valid. Again, having more definitive information on the porosity would be helpful.

As the time dependency of zinc concentration for Model C is the same for Model A, the Model-C treatment does not alter the apparent lag of outgassing in the early stages of the experiment relative to that predicted.

The important distinction between Model C and Model B is that with the former, granule size is an important factor in the rate of outgassing whereas in the case of Model B, the larger granules obtained in production (800-1000 $\mu$ m) would be expected to outgas at the same rate as those (~400 $\mu$ m) used in the outgassing experiments.

Thus, despite its limitations, Model C was used<sup>(12)</sup> as a granule-size-dependent model to treat the experimental data and to extrapolate the results to a production situation, i.e., outgassing of larger particles at higher temperatures, up to 1100 C, above which sintering of the granules becomes a problem.

The results of this extrapolation are given in Table 7 for granules initially containing 250 ppmw of zinc. The times to reach zinc levels of 25 and zero ppmw at 1050 and 1100 C are given. As can be seen from this treatment, if Model C is valid, hundreds of hours of heat treatment would be required for the granules expected to result from a commercial process.

#### General Discussion of the Outgassing Experiments

The major objective of the present work was to facilitate the extrapolation of outgassing data obtained on the Miniplant product to the larger granules expected to be characteristic of a commercial operation. Unfortunately,

TABLE 7. TIMES TO OUTGAS GRANULES IN ACCORDANCE WITH MODEL C

Residual Zinc, ppmw	Temperature, C	Time, h, to Outgas for Stated Granule Radius, $r_1$			
		200 $\mu$ m	300 $\mu$ m	400 $\mu$ m	500 $\mu$ m
25	1100	153	394	72	1146
	1100	34	88	162	257
0.0	1000	229	633	1217	1966
	1100	51	142	273	441

$r_s = 75 \text{ m}$ ,  $r_1 = \text{variable}$ ,  $\bar{C}_1 = 250 \text{ ppmw}$

For 1000 C,  $T = 1273\text{K}$ ,  $P' = 2.341 \text{ atm}$ ,  $D' = 2.3 \text{ E-7 cm}^2 \text{ s}^{-1}$

For 1100 C,  $T = 1373\text{K}$ ,  $P' = 5.178 \text{ atm}$ ,  $D' = 5.1 \text{ E-7 cm}^2 \text{ s}^{-1}$

where  $r_s = \text{seed radius}$

$r_1 = \text{granule radius}$

$\bar{C}_1 = \text{initial Zn concentration averaged over granule}$

$P' = \text{equilibrium vapor pressure of zinc}$

$D' = \text{permeability (having dimensions of diffusivity)}$

several uncertainties and inconsistencies remained in the results which would take more work to resolve than would be justifiable for this peripheral problem. However, the bulk of the evidence points to the existence of a connected porosity in the product that would favor rapid outgassing of the granules.

Table 7 is a "worst case" scenario, i.e., diffusion-limited transport from the interior to the outer surface of the particle. It is clear that outgassing times of the order of hundreds of hours would be required for granules of a practical size if diffusion from the body to the outer surface is limiting. However, if venting of the interior of the granules through a non-limiting network of pores is permitted, it may take no longer to outgas 800 $\mu$ m-diameter granules than it took to outgas the granules that were employed experimentally, that is, of the order of tens of hours.

Obviously, as the granule size is further increased, a point would be reached, beyond which transport through the connected porosity will become limiting. However, it is believed that the present data indicate tens of hours rather than the hundreds of hours outgassing times for e.g., 800 $\mu$ m-diameter granules.

The only way to confirm this prediction would be to measure the zinc evolution from granules significantly larger than those employed in this work. It was hoped that such granules would be available from the PDU operation. Unfortunately, such was not the case.

When such work is eventually done, it would still be of interest to study the outgassing as a function of time to detect the sudden levelling off of zinc removal that would be associated with the presence of residual zinc in compound form such as was suggested by the results of one experiment of the present work. It would also be of interest to investigate the porosity of the granules more thoroughly and relate this to the possible outgassing mechanisms (1) diffusion of elemental zinc through silicon and (2) reaction of silicon with zinc oxide.

### Vaporization of Zinc

One of the major advantages of the zinc-reduction process is that, except for a few volatile impurities such as cadmium (which, like zinc, will not be retained by molten silicon during initial cell processing), harmful impurities such as titanium have negligibly low vapor pressures at the boiling point of zinc, and except for possible entrainment in zinc mist, are left behind in the boiler. Misting must be minimized in any event, as it has been shown that surfaces of condensed zinc in contact with  $\text{SiCl}_4(\text{g})$  favor the nucleation of silicon needles which, if grown on zinc mist particles, would be entrained, and carried out of the fluidized bed, thus not becoming part of the dense product heterogeneously deposited on the silicon seed granules.

Two experiments were run, in each of which about 50 percent of a sample of zinc was volatilized and condensed, and the initial material, condensate, and residue were analyzed for iron, lead and cadmium to determine the volatility ratios. When these are compared with those expected from the relative vapor pressure of the components, they can give either (1) confidence in the purification obtained at that point, or (2) evidence for misting.

The relative volatility  $\alpha$  of the components of a binary solution, e.g., iron in zinc can be expressed as:

$$\alpha = \frac{(C_{\text{Fe}})_v}{(C_{\text{Fe}})_l} = \frac{\gamma_{\text{Fe}} p_{\text{Fe}}}{\gamma_{\text{Zn}} p_{\text{Zn}}}$$

where  $(C_{\text{Fe}})_v$  is concentration of iron in zinc condensate

$(C_{\text{Fe}})_l$  is concentration of iron in liquid zinc "heel"

$\gamma$  = activity coefficient in solution

$p$  = equilibrium vapor pressure of pure component

These equations are for instantaneous values, i.e., differential values in a system whose composition varies with the amount of material distilled. To

obtain the value of  $\alpha$  from the composition of the starting material and heel requires mathematical integration. Hultgren et al (16) give  $\gamma_{Pb}$  in zinc at 0 percent Pb = 34.6 at 923 K,  $\gamma_{Cd}$  in zinc at 0 percent Cd = 4.15 at 800 K. No data are given for iron but  $\gamma_{Fe}$  is equal 10. It is further assumed that the activity coefficient values are also valid at the boiling point of zinc, 1181 K.

These activity coefficients and published values of the vapor pressures lead to the following values of the relative volatilities to be expected:

$$\alpha_{Zn/Fe} = 10^9$$

$$\alpha_{Zn/Pb} = 64$$

$$\alpha_{Cd/Zn} = 3.5$$

In light of these values, no iron should be found in the condensed vapor, very little lead should be found, and the cadmium should be observed to vaporize preferentially.

Table 8 gives the results of the first experiment.

TABLE 8. DATA AND CALCULATED RELATIVE VOLATILITIES, EXPERIMENT A.

Item	Weight, g	Composition, ppmw		
		Fe	Pb	Cd
Initial Material	414.2	174	14	5
Condensate	231.4	28	8	6
Heel	182.8	423	24	<0.5

Ratio	$\alpha$ Theoretical	$\alpha$ Calculated	
		Initial vs. Heel	Initial vs. Condensate
Zn/Fe	$10^9$	*	8
Zn/Pb	64	3.0	2.5
Zn	16	3	3.5

\* Spurious negative value due to poor material balance; iron apparently generated in heel.

A spurious negative value of  $\alpha_{Zn/Fe}$  is obviously due to a poor material balance, and although the condensate is lower in iron than the starting material or heel, much more iron reached the condensate than would be expected.

The problem with the material balance is evident from an evaluation of the total amount of the respective element present in the condensate and heel relative to that present in the initial material. The values for the data of Table 14 are Fe = 1.16, Pb = 1.08, and Cd = 0.72.

On the assumption that better results would be obtained if the condensate and heel were sampled as liquids and not allowed to freeze before sampling (which could lead to segregation), a second experiment was carried out with the materials being sampled while still liquid and presumably homogeneous. The results are given in Table 9.

TABLE 9. DATA AND CALCULATED RELATIVE VOLATILITIES, EXPERIMENT B.

Item	Weight, g	Composition, ppmw		
		Fe	Pb	Cd
Initial Material	235.2	1.9	0.2	0.06
Condensate	128.7	1.4	0.2	0.03
Heel	105.6	6.7	0.3	<0.02

Ratio	$\alpha$ Theoretical	$\alpha$ , Initial, Heel	$\alpha$ , Initial, Condensate
Zn/Fe	10 <sup>9</sup>	*	1.5
Zn/Pb	64	2	1.0
Cd/Zn	16	>1.8	<1

Again, excessive amounts of iron and lead found their way to the condensate, and a poor material balance resulted in the apparent creation of iron in the heel. The total element in condensate plus heel relative to the starting material was Fe = 1.99, Pb = 1.22, and Cd 0.42. With such discrepancies in the material balance, it is not possible to calculate reliable values of the relative volatility. However, the qualitative evidence for excessive volatilization of the iron and lead suggests that mechanical carry-over of these elements was taking place and that further study should be made of this question with the vaporizer actually being used in the PDU so that its degree of mist generation could be assessed. As the progress with the PDU did not permit it, such a study remains to be done.

#### Direct Coupled Zinc Vaporizer

As noted earlier, technology for the metering of zinc vapor at atmospheric pressure is believed to be non-existent. Accordingly, the zinc feed system used in the Miniplant consisted of a motor-driven piston for displacing zinc from a cylinder into an induction-heated graphite-tray vaporizer. When consideration was given to the scale-up of such a system, it was recognized that because of the high thermal capacity of the graphite tray and appreciable inventory of liquid zinc in the vaporizer, considerable hysteresis would be involved in the response of the zinc vapor flow to a change in the rate of liquid flow. To avoid this hysteresis, the concept of direct coupling of r.f. energy to the zinc was explored.

Early experiments with this concept recorded in the Phase I/II Final Report<sup>(1)</sup> led to adoption of the vaporizer shown in Figure 11 for the PDU design. However, as noted in the PDU activities section of this report, peculiarities in the wave form of the r.f. power (high voltage peak on initiation of pulse) led to the formation of a parasitic plasma in the zinc vapor. Accordingly, the less desirable tray-type vaporizer was installed in the PDU as an operating expedient, while efforts were made to evaluate the direct-coupled vaporizer independently.

Owing to the pressure of work with the PDU, the direct-coupled vaporizer concept was only partially evaluated. However, the important determination was made, that, in contrast with the plasma-forming behavior of the induction

unit that had the electronic power pulse control, no plasma was observed with the unit having a saturable core-reactor control. It was therefore concluded that future use of the direct-coupled vaporizer should be with a saturable-core-reactor-controlled r. f. generator.

#### Segregation of "Large" Particles in the Fluidized-Bed Reactor

Experiments with a model of the fluidized-bed reactor of the EPSDU/PDU design were described in the Phase I/II Final Report<sup>(1)</sup>.

Work on the fluidized-bed model during the present report period was limited to the question as to whether or not segregation by particle size could be induced so that preferential withdrawal of the larger particles might occur and plugging of the product-withdrawal tube by excessively large particles might be avoided.

As discussed in that report, segregation apparently results in areas where the velocity of the incoming gas is below the minimum for fluidization of the large particles and where the circulation of the small particles into the area is insufficient to impart their kinetic energy to the large particles and move them out. Such a condition is established in the "boot" zone\* of the fluidized bed being studied by U.C.C. (17) and has been observed to a limited extent at BCL in other bed-support geometries which have gas-velocity transition regions near the inlet (conical inlet, etc.)

Experiments aimed at detecting segregation were carried out in the transparent mock-up of the PDU fluidized bed described in the Phase I/II Final Report<sup>(1)</sup> which has the bed support plate shown in Figure 18. The dummy bed was of sea sand having the particle size distribution of a "mature" bed, shown in Table 10. The fluidizing gas was air and the velocity was that judged qualitatively to give the degree of bed activity characteristic of the Miniplant operation and the projected PDU operation. The bed was withdrawn at the average rate of 50-60 g/min required of the PDU operation. This average was obtained by fully opening the withdrawal tube 1 out of every .5 seconds (actual intermittent product withdrawal rate = 750-900 g/min).

When only limited, if any, segregation was observed in the initial experiments, a few large "marbles" (3000-4000 $\mu$ m, about 0.1 percent of the bed)

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\* Decreased-diameter, high-gas-velocity section at bottom of reactor.

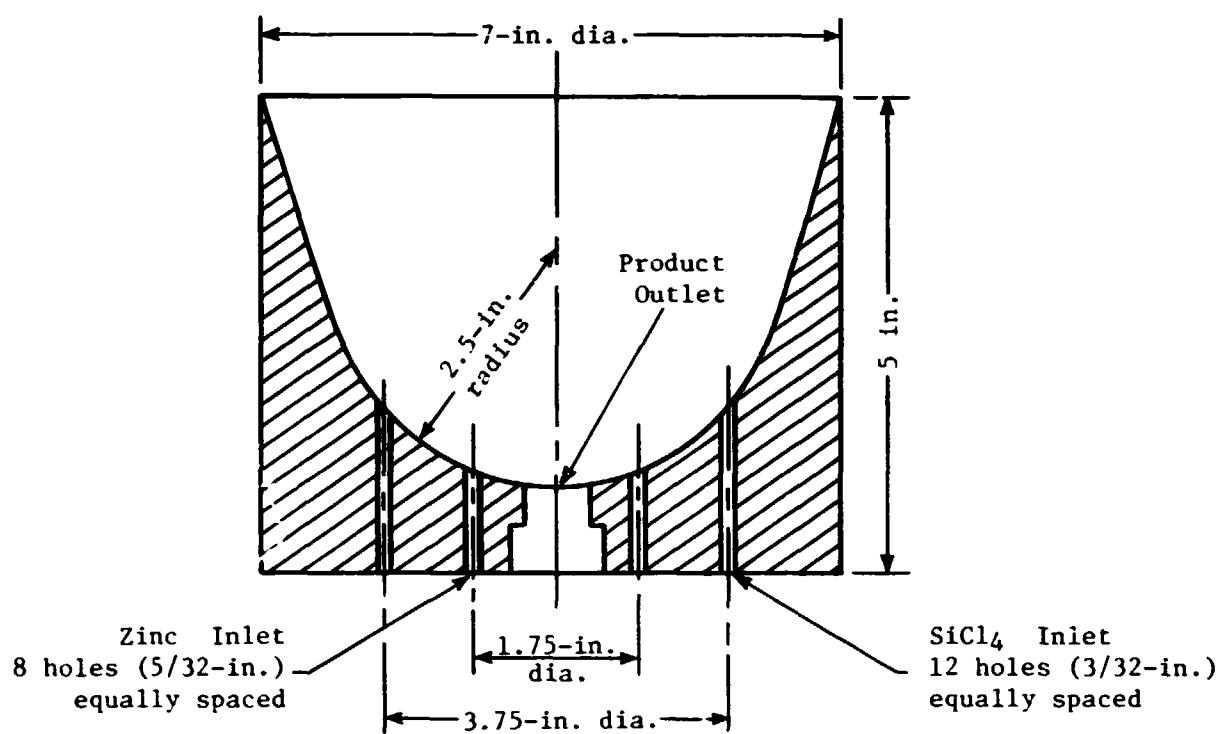


FIGURE 18. DIAGRAM OF ROUND-BOTTOM DISTRIBUTOR  
USED IN MODEL STUDIES

TABLE 10. PARTICLE SIZE DISTRIBUTION FOR SEGREGATION  
EXPERIMENTS IN FLUIDIZED-BED MODEL.

Particle Size Range, $\mu\text{m}$	Weight Percent
105-149	3.5
149-210	6.5
210-279	16.9
279-420	19.5
420-590	32.0
590-840	16.5
840-1000	3.5
1000-1190	1.3
1190-1410	0.3

were added to widen the spread of particle size. Again, no clear evidence of segregation was observed.

At one point in the experiments some segregation was observed that was correlated with the rate of purge gas flow through the product withdrawal tube. In the light of the U.C.C. experience<sup>(17)</sup>, it is believed that the product withdrawal tube was acting as a "boot" and that segregation was occurring within the product withdrawal tube itself and not in the fluidized bed.

At high enough purge gas velocity in the product withdrawal tube it should be possible to preferentially elutriate small particles from that region and thus promote segregation. However, the initial intention was to avoid such high flows and their cooling effect on the bed. Within that framework it was concluded that no appreciable segregation could be anticipated in the fluidized bed under the projected operating conditions.

It should be noted that the incentive to promote segregation in the PDU/EPDSU operation is limited as long as the prospect remains of discharging the entire bed weekly to chlorinate the wall deposit, at which time the larger particles can be easily removed. However, if the necessity of periodically chlorinating the wall deposit decreases, it would be desirable to explore fully the implications of operating the product withdrawal tube periodically at high purge velocities to promote segregation.

#### Electrolysis of $\text{ZnCl}_2$

As discussed above and in the Phase I/II Final Report<sup>(1)</sup>, the intention has been to utilize the experience of the Bureau of Mines, Reno, Nevada<sup>(7, 8)</sup> in the design and operation of the cell for electrolysis of  $\text{ZnCl}_2$  for zinc and chlorine recycle. However, experiments have been carried out in the present program to confirm the experience of the Bureau of Mines and to account for differences in the two situations, such as the necessity in the present program of chlorinating the small quantities of finely divided elemental silicon that are expected to find their way to the electrolytic cells.

Prior work with the electrolysis of the zinc chloride by-product of prior Miniplant operation led to the following major conclusions:

- (1) The Miniplant by-product condensate can be electrolyzed to recover zinc and chlorine from the contained  $\text{ZnCl}_2$  without apparent interference (such as cell shorting) by the contained suspended zinc and silicon dust.
- (2) Silicon dust suspended in the by-product condensate can be chlorinated in the electrolytic cell at least up to 3.4 percent of the silicon production of the fluidized bed.
- (3) Cell voltages were higher\* than those experienced by the Bureau of Mines work. This is believed to relate partly to electrode resistance loss and perhaps to less efficient mixing of the  $\text{ZnCl}_2$  with the KCl electrolyte inventory. Solution of this problem was being pursued.
- (4) The projected electrical energy requirement of about 2 kWh per pound of zinc electrolyzed\* appeared to be reasonable.

Although runs with current efficiencies of the expected 95 percent were made in the prior work<sup>(1)</sup>, the current efficiency sometimes fell short, and the power efficiency, around 20 percent, was consistently below the ~36 percent obtained by the Bureau of Mines in a small cell and projected for their 50,000-amp cell.

In an effort to learn more about the system and to raise the power efficiency if possible, a more flexible closed cell was designed in which the entire electrode assembly was brought in from the cell cover so that it could be immersed in the 55 m/o  $\text{ZnCl}_2$ -45 m/o KCl electrolyte contained in a 1000-cc Pyrex beaker. To minimize the change in cell characteristics during the electrolysis, no more than 20 percent of the  $\text{ZnCl}_2$  was electrolyzed during any run so that the  $\text{ZnCl}_2$  concentration did not drop below 49 m/o.

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\* It should be noted that the power consumption of 2 kWh per pound of zinc adopted for the power consumption in the economic evaluations of the process in this report (Tables 1 and 2) is conservative, corresponding to a power efficiency of only 29.3 percent.

Aside from the fact that the comparable Bureau of Mines experimental cell<sup>(7)</sup> was an open cell, the major difference in the cell used in the present work was the larger electrodes (8.9- vs 3.8-cm diameter) for which the removal of chlorine from the electrode area would be more difficult and shielding of the anode by chlorine gas bubbles potentially more of a problem. The graphite electrodes in the present cell were 8.8-cm diameter, near-horizontal plates, leaving 0.6 cm clearance at the container wall. Rather than to complicate the cell cover design by using massive electrodes, graphite rods of convenient size were used to make the connections to the anode and cathode. The calculated IR drop in these leads (e.g., 2 V at 45 amp) was subtracted from the measured cell voltage in determining the power efficiency of the cell.

The first group of experiments with electrodes of different configuration and spacing are summarized in Table 11. The major objective of these experiments was to explore the effect of enhanced chlorine removal and electrolyte circulation on the power efficiency of the cell. Although a number of changes in electrode design were made, the effects of the changes on the initially improved, 30 percent, power efficiency were so small (in most cases 1 to 2 percent) as to possibly be within experimental error and make difficult the correlation of any real but minor effect.

Although one might attempt to draw a conclusion from a comparison of the results of Runs 2 and 3 regarding the effect of slotting the inclined electrodes, the presence of other variables clouds the picture. Although the slotting should decrease gas-bubble shielding of the anode by facilitating the removal of chlorine, increasing the current density acts in the opposite direction. The temperature difference may also have an effect [expected 5 relative percent decrease in power efficiency<sup>(7)</sup>]. Further, the low current efficiency in Run 2 is hard to explain in the light of prior and subsequent experiments in which current efficiencies were consistently above 90 percent. In this case, a problem was experienced with recovery of the zinc product which may account for the low current efficiency. It is probably advisable to discount the results of Run 2.

The effect of perforating the anode (Run 4) to aid in the chlorine release was in the direction expected, i.e., an increase in both current and power efficiency.

TABLE 11. SUMMARY OF ZnCl<sub>2</sub> BY-PRODUCT ELECTROLYSIS  
EXPERIMENTS AT 500 C (a)

Run Number (b)	Electrode Configuration	Electrode Spacing, cm	Current Density, amp/cm <sup>2</sup>	Power Efficiency, percent	Current Efficiency, percent	Average Temperature, C
2	Planar electrodes inclined 4 degrees	1.27	0.59	31.9	86.1	477
3	4 degree inclined electrodes, 8 degree slotted anode (c)	1.27	0.72	28.0	93.7	501
4	4 degree inclined electrodes, 8 degree slotted and perforated anode	1.27	0.76	30.9	95.3	492
5	4 degree inclined electrodes, 8 degree slotted and perforated (d) anode, forced gas purge (e)	1.27	0.76	30.7	95.1	502
6	12 degree inclined planar electrodes	1.27	0.80	31.8	95.1	503
7	12 degree inclined planar electrodes	1.90	0.75	31.5	96.1	504

- (a) ZnCl<sub>2</sub> by-product of the Miniplant, containing approximately 78 percent ZnCl<sub>2</sub>, 21 percent zinc, and 0.7 percent Si; admixed 55 m/o with 45 m/o KCl.  
 (b) In Run 1, the cell temperature range was excessively broad, so the data are not included.  
 (c) Four 0.32-cm rectangular grooves in the direction of incline, spaced 1.6 cm, the "bottom" of the grooves inclined at degrees to horizontal.  
 (d) 0.32-cm-diameter holes through anode at 1.27-cm intervals along the grooves.  
 (e) Argon purge of underside of anode ~3X rate of Cl<sub>2</sub> evolution.

In Run 5, the effect of bringing in a purge gas (argon) under the low side of the anode to increase salt circulation\* was investigated. No net effect was observed. Thus, if any advantage was gained from increased salt circulation it may have been offset by increased shielding of the anode by the additional gas.

Increasing the inclination of the electrodes to 12 degrees to horizontal (the maximum that can be accommodated in the EPSDU electrolytic cell design) appears to have been beneficial despite the absence of grooving and perforation. Increasing the electrode spacing from 1.27 to 1.9 cm decreased the power efficiency by only 1 relative percent (five relative percent decrease was recorded at the Bureau of Mines<sup>(7)</sup> in 13 m/o  $\text{ZnCl}_2$ -36 m/o  $\text{KCl}$ -51 m/o  $\text{LiCl}$  under otherwise comparable conditions).

In the second group of experiments, Table 12, the major variables investigated were the current density, slant of the electrodes, and electrode-to-wall clearance, the latter two factors being of potential importance in the release of chlorine gas from underneath the anode.

Two runs (18 and 20) were made at different times under base-line conditions:

4-degree-inclined planar 8.8-cm-diameter electrodes,  
no grooves or holes, Salt Mix II, 1.27-cm electrode  
spacing, 0.80 amps/cm<sup>2</sup> current density, and 499-502 C  
temperature.

The current efficiency values averaged  $95.2 \pm 1.5$  amps/cm<sup>2</sup> and the power efficiency,  $36.3 \pm 0.6$  percent. Decreasing the electrode area by 25 percent\*\* in Run 21 to increase the electrode-to-wall clearance had the effect of increasing the power efficiency slightly (to 37.9 percent) in the direction expected for an increase in the ease of chlorine evolution and electrolyte circulation.

The highest power efficiencies (38.7 and 42.5 percent) were obtained in Runs 12 and 17, respectively, in which the greatest opportunity was provided for chlorine release (12-degree slant, perforated anode, 25 percent reduced area).

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\* Directed toward decreasing possible local  $\text{ZnCl}_2$  depletion. Argon was introduced at about 3 times the volumetric chlorine generation rate.

\*\* Two segments sliced off circular anode along parallel symmetrical chords 3.2 cm apart.

TABLE 12. SUMMARY OF ADDITIONAL  $ZnCl_2$  BY-PRODUCT  
ELECTROLYSIS EXPERIMENTS AT 500 C(a).

Run Number(b)	Electrode Configuration	Electrode Spacing, cm	Current Density, amp/cm <sup>2</sup>	Power Efficiency, percent	Current Efficiency, percent	Average Temperature, C
11	12-degree-inclined planar electrodes, Salt Mix I	1.27	0.79	35.6	96.5	502
12	12-degree-inclined planar electrodes, Salt Mix I, 25 percent reduced area, perforated anode(c)	1.27	0.79	38.7	96.2	503
17	12-degree-inclined planar electrodes, Salt Mix II, 25 percent reduced area, perforated anode(c)	1.27	0.80	42.5	99.5	499
18	4-degree planar baseline electrodes, no grooves or holes, Salt Mix II	1.27	0.80	36.9	96.7	502
19	12-degree-inclined planar electrodes, 25 percent reduced area, no grooves or holes, Salt Mix II	1.27	1.58	30.8	100.1	512
20	4-degree-inclined planar baseline electrodes, as No. 18, Salt Mix II	1.27	0.80	35.7	93.7	499
21	4-degree-inclined planar baseline electrodes, as No. 18, Salt Mix II 25 percent reduced area	1.27	0.79	37	93.6	499

(a)  $ZnCl_2$  by-product of the Miniplant. Salt Mix I contained ~98.9 percent  $ZnCl_2$ , 0.1 percent Zn, and 1.0 percent Si (miniplant by-product had been heated above the melting point of zinc to settle out the suspended zinc), admixed 55 m/o with 45 m/o KCl. In Salt Mix II, the Zn and Si contents were ~7.8 and ~2.2 percent, respectively.

(b) Runs Nos. 8 through ten and 13 through 15 are not included because of minor technical problems which made the data suspect

(c) 2.4-mm holes spaced 13 mm apart in hexagonal array.

The results of Run 11 with 12-degree tilted planar (unperforated) electrodes were not above baseline. However, it is believed that uncontrolled variables (mix inhomogeneity?) masked the real effect of the increased tilt (12 degrees vs 4 degrees). The presence of such uncontrolled variables is indicated by the incidence of two current efficiencies unrealistically high in the neighborhood of 100 percent (Runs 17 and 19).

The decreased power efficiency in Run 19 to 30.8 percent (compare Run 17, 42.5 percent) can be attributed to doubling the current density.

On the basis of these results, the 12-degree slant (actually 11 degrees, i.e., maximum tolerable within the cell) was adopted for the PDU design. Initial plans were to use an unperforated anode and to carry out experiments with a perforated electrode later. However, that change was actually not made.

#### Wetted-Wall Condenser Studies

The by-product from the fluidized-bed reactor of the PDU/EPDSU design is a unique mixture consisting nominally of the following (per one 25 MT Si/year fluidized-bed reactor):

Si dust	0.16 lb/hour
SiCl <sub>4</sub> (g)	29.61 lb/hour
Zn(g)	22.77 lb/hour
ZnCl <sub>2</sub> (g)	80.87 lb/hour
Ar	1.15 lb/hour.

This mixture leaves the reactor at ~925 C. If it were gradually cooled, and no reaction occurred, the bulk of the zinc (86.4 percent) would condense out by the time the temperature reached 766 C, near which temperature the ZnCl<sub>2</sub> would start to condense out with 99.3 percent of the ZnCl<sub>2</sub> and 99.8 percent of the zinc having condensed by the time the temperature reached 527 C<sup>(1)</sup>, still well above the melting point of zinc (420 C) and ZnCl<sub>2</sub> (318 C). However, if this by-product mixture were allowed to cool gradually, the unreacted SiCl<sub>4</sub>(g) would react with the unreacted Zn(g) to form additional silicon\* in the condenser, which, added to the 0.16 lb/hour of dust already in the by-product, would probably exceed the capacity of the electrolytic cell to chlorinate it.

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\* The equilibrium efficiency of the reaction  $\text{SiCl}_4(\text{g}) + 2\text{Zn}(\text{g}) = \text{Si}(\text{s}) + 2\text{ZnCl}_2(\text{g})$  increases with decreasing temperature.

C-2

Hence, the by-product mixture must be quenched to prevent further reaction.

The wetted-wall condenser, in which liquid  $\text{ZnCl}_2$  is recirculated to wet the condensing surface, was designed to accomplish the condensation in such a way as to have the following advantages:

- (1) Operation of the condenser surface at 350 C would effectively quench the by-product mixture and prevent further silicon formation.
- (2) Operation below the melting point of zinc permits keeping the condensed finely divided solid zinc in suspension in the  $\text{ZnCl}_2$  until the  $\text{Zn}/\text{ZnCl}_2$  mixture is heated to above the melting point of zinc in the electrolytic cell, where the zinc coalesces.
- (3) Operation at 350 C permits use of stainless steel in contact with the zinc (finely divided solid) without the swelling of the metal encountered above the melting point of zinc.

It is essential that the flow of re-circulated  $\text{ZnCl}_2$  be sufficient to prevent drying of the wetted wall, otherwise accumulation of silicon dust or zinc powder would constrict the condenser.

Although wetted-wall columns are used for condensation and absorption in industry, none is known to operate under the requirements of EPSDU, and the chances of finding useful information that is directly pertinent are regarded as slim. Accordingly, an experiment was devised in which the product of the Miniplant (which should be representative of that expected from the EPSDU/PDU) was fed into a wetted-wall condenser, patterned in principle after that of the EPSDU/PDU design but of smaller size.

In the EPSDU/PDU reactor condenser design (Figure 12 of this report), condensation occurs in three parallel 1.5-inch-diameter 10-ft-long channels at 350 C at a linear flow rate of 8.2 fps. In the Miniplant wetted-wall condenser assembled for the independent study, a single 1-inch-ID tube 6 feet long was provided.

In scaling the EPSDU condenser down to the Miniplant size, one must consider gas flow velocity in the tubes, Reynolds number, heat transfer area, and flow of  $\text{ZnCl}_2$  per unit surface area, as well as total tube perimeter.

Since it was obviously impractical to proportionally scale all of these factors, it was necessary to select those which were thought to contribute most to the condenser operation. After these factors were reviewed with RKAI, it was decided that the most practical approach to sizing which should provide useful information would be based on surface area. In addition, it would be best if the Miniplant condenser was undersized so that its condensing capacity limit might more easily be determined. Accordingly, the area of the Miniplant condenser was chosen to be only about 70 percent of that which would result from a direct size reduction based on plant production rates.

The nominal flow rate of liquid zinc chloride to the wetted wall of the miniplant condenser was chosen to be essentially that designed for the EPSDU condenser in terms of quantity per unit of condenser area, or 0.2 gallons per minute for the 1-inch-diameter tube. Provisions were made to vary the zinc chloride flow rate, to obtain some idea as to the minimum quantity needed to maintain a wetted wall. With this information, the amount supplied in practice could then be confidently held in excess of the minimum, so as to prevent a dry wall condition and subsequent choking-off of the condenser tube.

Figure 19 is a schematic diagram showing the major features of the wetted-wall condenser. The by-product mixture used to evaluate the condenser was generated by a Miniplant reactor similar to that pictured in Figure 1e of the Phase I/II Final Report<sup>(1)</sup>, except that the zinc vapor was routed to the axial inlet with the  $\text{SiCl}_4$  introduced from the four surrounding inlets, as had been the practice from Run 56 on in the Miniplant to avoid silicon deposition on the orifice plate.

Duplication, in the experimental condenser, of the Reynolds number (4100) at which the gases enter the condenser of the PDU would have required the use of a tube less than 0.4 inch in diameter and over 17 feet in length, depending upon the output of the miniplant. Since this was thought to be overly constricted and would require more head room than was available, a rationale was sought for using a larger diameter tube that would not only decrease the danger of flooding or constriction, but would permit the use of a shorter tube for the same surface area.

By the time about 50 percent of the zinc and zinc chloride have condensed, the Reynolds number for flow in the PDU condenser will have dropped out of the transitional range ( $\text{N}_{\text{Re}} = 4100$ ) into the laminar flow range

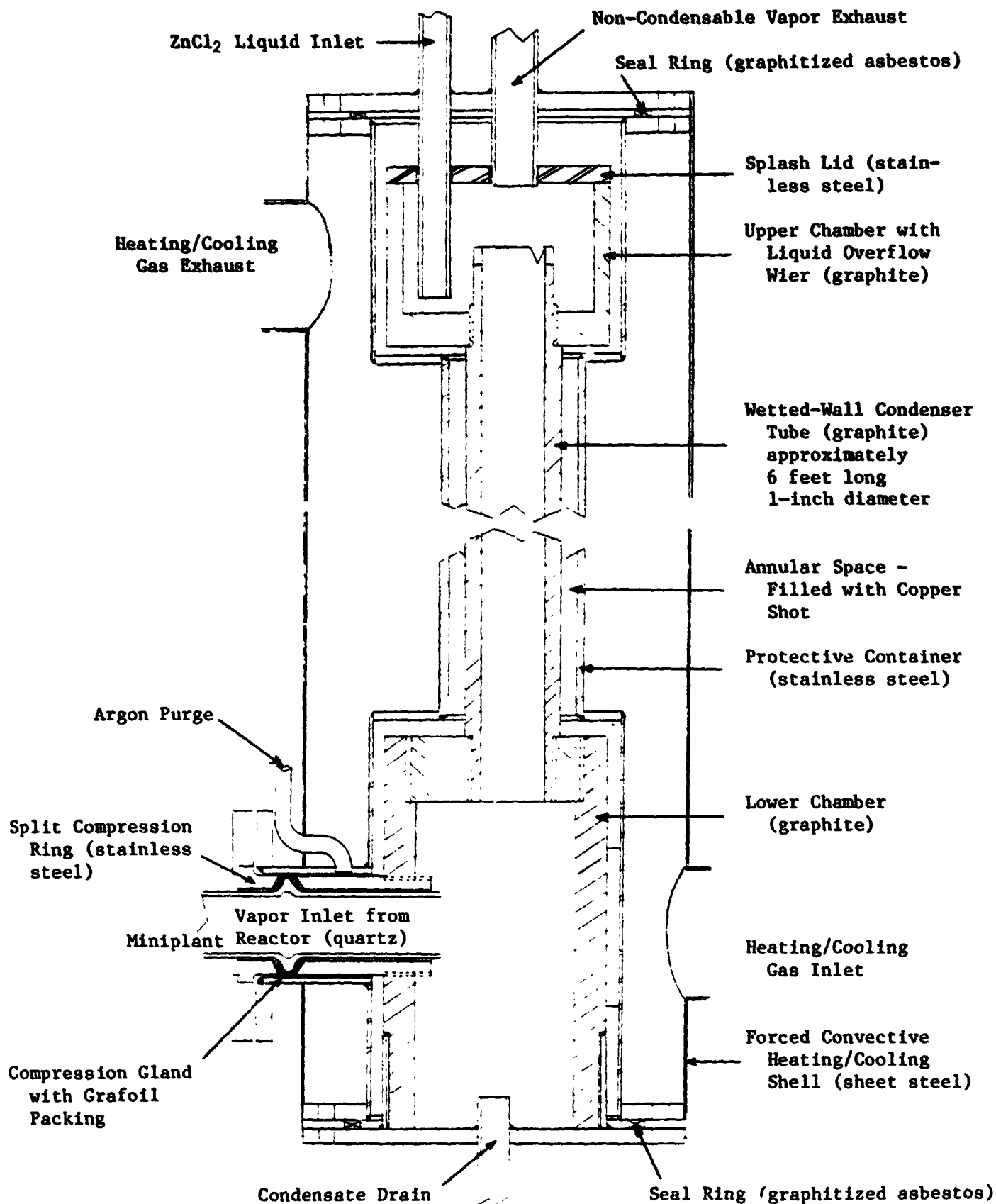


FIGURE 19. SCHEMATIC DIAGRAM OF LABORATORY-SCALE WET-WALL CONDENSER

SCALE: 1/2" = 1"

( $N_{Re} = 2500$ ). Under these conditions, the flow rate would not be expected to have a great effect on condenser efficiency at constant area per unit throughput. Hence, the adoption of the 1-inch-ID\* by 6-foot-long condenser tube was believed to be justified.

Flow of  $ZnCl_2$  to the condensing surface of the mock-up was provided by use of interchangeable  $ZnCl_2$  reservoirs which, depending upon the  $ZnCl_2$  flow chosen, provided for runs of about 1-hour duration\*\*. The initial run was made with pure  $ZnCl_2$  drained from the upper reservoir to the lower. Subsequent runs were made with  $ZnCl_2$  containing increasing amounts of suspended zinc and silicon dust as the positions of the reservoirs were interchanged. The reservoirs were of about 16-gallon capacity so that, starting with one containing ~8 gallons of  $ZnCl_2$ , about 20 1-hour runs would be required to add  $ZnCl_2$  (+Zn + Si) to the point of reaching the capacity of the reservoir, at which time the concentration of zinc and silicon\*\*\* would have reached about 45 percent of that in the 950 C equilibrium by-product mixture. As this amounts to only 4.5 percent zinc in the  $ZnCl_2$ , the fluidity should not be prohibitively changed; however, data on the apparent viscosity of the mixture as a function of zinc concentration and particle size have not been obtained.

The first two 30-minute runs in the condenser mock-up assembly proceeded smoothly with good indication by borescope examination that the wetted-wall principle was effective in clearing the condenser surface of silicon and zinc solids. It was observed, however, that, due to inadequate condenser cooling masked by a deficiency in the gas-temperature monitoring arrangements, excessive amounts of  $ZnCl_2$  were escaping the condenser. With improved positioning and shielding of the gas temperature thermocouple, several runs were made to establish the proper condenser cooling conditions. However, overcooling at the bottom (inlet) end of the condenser led to constriction and flooding of the fluidized-bed reactor with  $ZnCl_2$ .

Later, successful operation of the wetted wall condenser mock-up demonstrated that temperature control in the condenser and control of the temperature distribution at the inlet end of the condenser was fairly critical

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\*  $N_{Re} = 1000$ .

\*\* The capacity of the zinc reservoir limited the run time.

\*\*\* Finely divided zinc is the major component, the volume of the finely divided silicon is about 2 percent that of the zinc on a fully dense basis.

thus explaining the problems experienced with earlier runs. Fortunately, temperature control was anticipated to be less critical with the full-scale PDU/EPSDU condenser.

Although undoubtedly open to further improvement, the collection efficiency of the  $\text{ZnCl}_2$  and zinc was much improved over that obtained in the earlier runs, as judged from the materials collected in a room-temperature glass-wool-packed back-up trap for the condenser. On the assumption of 63 percent conversion of  $\text{SiCl}_4$  to silicon in the Miniplant section, the wet-wall condenser collected approximately 92 percent of the  $\text{ZnCl}_2$  formed and 97 percent of the residual zinc vapor. It was anticipated that the carry-over of entrained materials would be decreased in the PDU wetted-wall condenser design since the gas stream changes direction in that condenser.

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